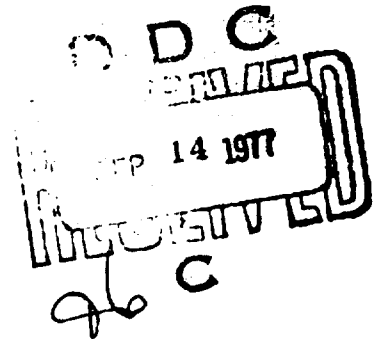# IMPROVED INTUMESCENT PAINT

Final Report
May 6, 1975 - October 5, 1976
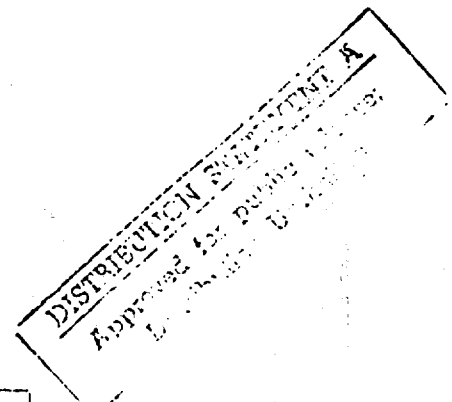
Issued February 7, 1977

Prepared under Contract No. N00024-75-C-4427
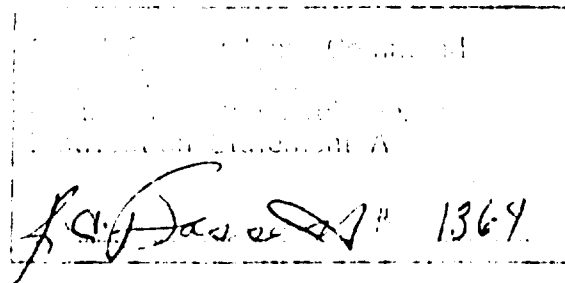for the Naval Sea Systems Command

David O. Bowen
Designed Products Department

Andrew T. Graham
Saran & Converted Products Research

The Dow Chemical Company
Midland, Michigan 48640

1 2 SEP 1977

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NOTE: Numerical flame spread ratings which appear herein are not intended to reflect hazards presented by these or any other materials under actual fire conditions. Flame-retardant coatings serve only to inhibit ignition and rate of flame spread. Treated materials which are otherwise combustible will burn.

IMPROVED INTUMESCENT PAINT

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IMPROVED INTUMESCENT PAINT
ABSTRACT

Formulation studies using commercial Saran microspheres and halogenated latex binder led to the development of aqueous intumescent coatings. When modified with certain flame retardant additives, compositions impart excellent flame spread resistance to wood substrates. Microsphere/latex compositions modified with decabromodiphenyl oxide provide good flame insulation properties for steel panels; panel backside temperatures remained below 1000°F during flame exposure of phosphatized steel panels coated with intumescent composition. Latex/microsphere intumescent coatings show good quality and appearance when applied to wood. Further work on primer systems is needed, however, to eliminate cracking and discoloration of coatings when applied to steel panels.

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IMPROVED INTUMESCENT PAINT

Introduction

The use of water-based intumescent coatings for fire protection in
fleet ships and submersible craft would offer obvious advantages
over currently-used solvent-based intumescent paints from the
standpoint of reduced fire and/or respiratory hazard during application
and drying of the coatings. While water-based intumescent coatings
have been studied previously[1], such systems ordinarily use water-
soluble formulation additives for proper foaming and char formation.
The tendency of such additives toward leaching upon repeated or
prolonged exposure of the coating to water leaves some question
as to the long-term intumescent capabilities of these systems.

This report presents results from feasibility studies based on
technology departing substantially from current state of the art
for intumescent paints. In these studies, novel water-based intumescent
coatings were prepared from combinations of (1) halogenated latex
binders with inherent char-forming ability and (2) thermally-expandable,
water-insensitive Saran[2] microspheres. With relatively mild heating,
the microspheres are capable of forming a foam[3] in the presence of
the halogenated binder, and are also capable of char-formation at
higher temperatures. When modified with certain formulation additives,
such compositions showed excellent fire protection characteristics
under laboratory flame exposure conditions.

Saran microspheres are based on a vinylidene chloride copolymer composition. The manufacturing process is such that a hollow, spherical particle is produced, with isobutane encapsulated inside the polymer shell to effect expansion of the particle when exposed to heat. As manufactured, the microspheres have an average particle size of about seven microns. Upon heating and expansion, average particle size is increased to about 28 microns, representing a sixty-four-fold increase in volume. Thermal expansion of saran microspheres is represented schematically in Figure 1. Also seen in Figure 1 are essential properties of a commercial microsphere product, designated as Experimental Resin XD-8217.00 and manufactured by The Dow Chemical Company. The halogenated binder used most often in the present work is a saran-type emulsion polymer designated Saran Latex 143, also available from The Dow Chemical Company. Properties of this thermoplastic film-forming latex product are listed in Table I.

Intumescent coatings developed in the present work are based on the hypothesis that an aqueous, halogenated binder could be modified with saran microspheres, applied to a suitable substrate, and air-dried at room temperature to give a continuous thermoplastic polymer film containing microspheres dispersed throughout the coating thickness. Upon exposure to heat, intumescence would result in a two-stage process, represented schematically in Figure 2. In the early stages of heating, softening of the thermoplastic binder and expansion of the microspheres would result in formation of halogenated syntactic polymer foam (Stage I). Upon

FIGURE 1
PROPERTIES OF
SARAN MICROSPHERES

VINYLIDENE CHLORIDE/ACRYLONITRILE POLYMER. HOLLOW, SPHERICAL
PARTICLE CONTAINING ISOBUTANE BLOWING AGENT.

UNEXPANDED   EXPANDED

POLYMER

ISOBUTANE   ∿95°C

AVG. DIAM   AVG. DIAM
6μ   25μ
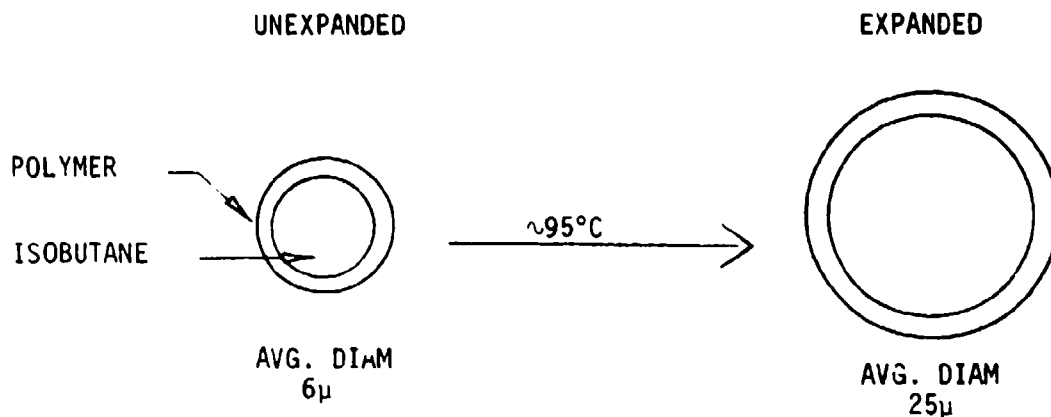
TYPICAL PROPERTIES, EXPERIMENTAL RESIN XD-8217
(UNEXPANDED WET CAKE)

SOLIDS CONTENT	60% AQ.
BULK DENSITY	45 LB/FT^3
TRUE DENSITY	83 LB/FT^3
PARTICLE SIZE, AVG. DIAM.	6 - 8 μ
PARTICLE SIZE, RANGE	4 - 20 μ

PROPERTIES AFTER EXPANSION

BULK DENSITY	<1 LB/FT^3
TRUE DENSITY	1.5-2.3 LBS/FT^3
PARTICLE SIZE, AVG. DIAM.	25-28 μ
PARTICLE SIZE, RANGE	10-80 μ

TABLE I
PROPERTIES OF SARAN LATEX 143

Type: High barrier Saran latex for coating glassine, paper and
paperboard.

Nature of Deposited Coatings: Clear, continuous, flexible, tough,
glossy, and non-tacky.

Typical Latex Properties:

Percent Solids	54
Specific Gravity, Wet Latex	1.30
Specific Gravity, Latex Solids	1.68
Pounds Latex Per Gallon	10.85
Surface tension, dynes/cm	56
pH of Latex	2
Latex Stability, HB, 18,000 rpm, Minutes	>30
Foaming Characteristics	Very Low

Typical Properties of SL-143 Coatings

6# total coating/3000 ft^2, applied in two equal coats, on 30# opaque
white glassine, each coat dried for 30 seconds at 300°F.

Flat WVTR, gms/100 in^2/24 hours

     95% RH & 100°F   0.4

Creased WVTR, gms/100 in^2/24 hours

     95% RH & 100°F   0.5

Heat Seal Temperature, 20 psi, 1 sec

     Ctg --------->Ctg   125°C (257°F)

FIGURE 2   PROPOSED MECHANISM FOR INTUMESCENCE IN SARAN MICROSPHERE/SARAN LATEX COATINGS
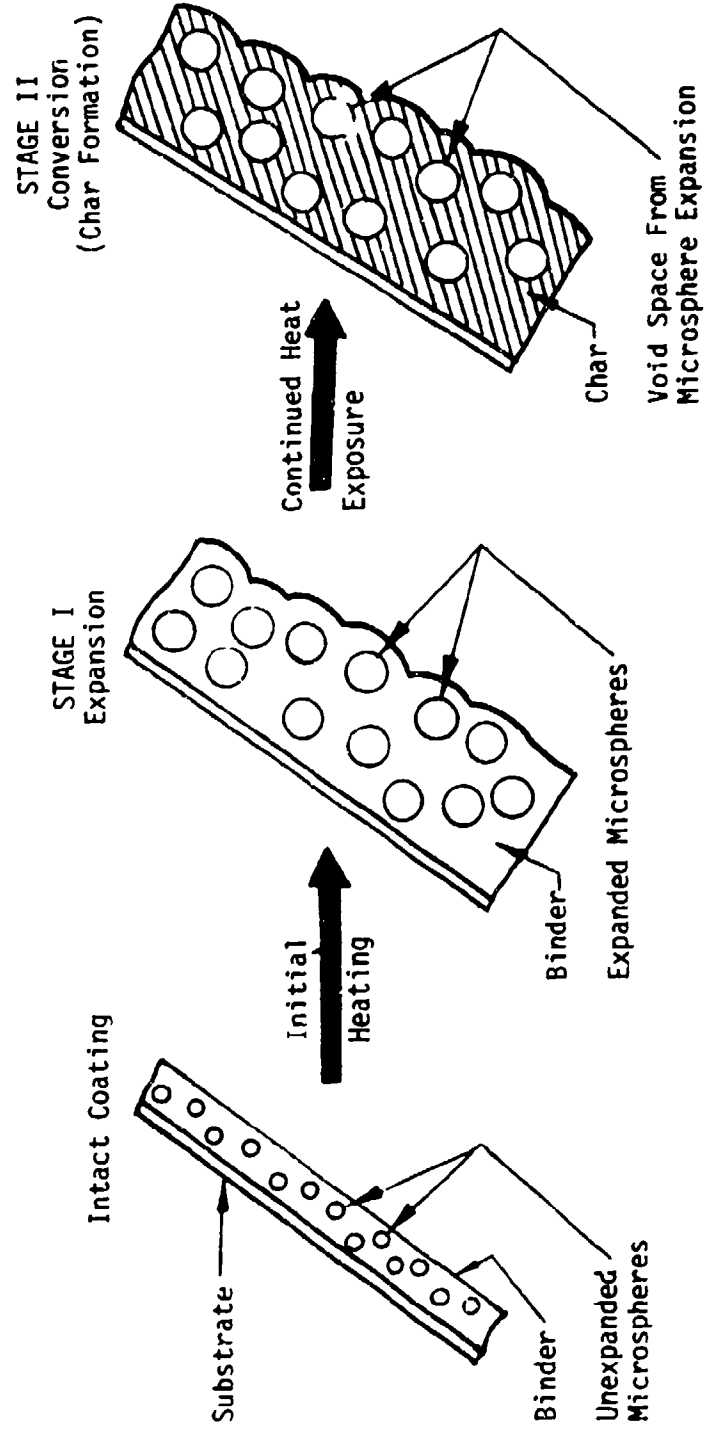
further heating, chemical compositions of both the latex binder and the
microsphere shell are such that dehydrohalogenation and char formation
take place to yield a carbonaceous, microvoid-containing char capable of
providing thermal insulation for the substrate (Stage II). In this
proposed two-stage system applied from water, solvent hazards are eliminated.
Water-soluble intumescent additives are not required, since the microspheres,
which act as an inert filler in the presence of water, serve as the foaming
agent and the binder itself serves as the primary char source.

Work carried out under the present contract has borne out the hypothesis
presented above, and water-dispersed intumescent coatings based on
halogenated latex and saran microspheres have been developed which,
when applied to steel substrates, offer a degree of thermal protection
comparable to that seen when using solvent-based MIL-C-46081 coatings.
Ancillary studies further show that such compositions may also serve
to significantly improve flame resistance of wood substrates.

With regard to other coating properties such as brightness, appearance,
adhesion, etc., compounds of the present work appear to be satisfactory
when applied to wood substrates. These properties are not considered
to be equal to those seen with solvent-based intumescent paints when
applied to metal substrates, however, and advanced development work for
improved coating quality would be recommended prior to commercial or
military use for fire protection of metal surfaces.

II. Program Objectives

The primary objective in this study was to determine whether combinations of saran microspheres with aqueous-based halogenated binder systems could be compounded into coatings which would impart thermal intumescent protection to steel substrates in a manner similar to that obtained when using solvent-based intumescent paints. A further objective was to develop water-based intumescent formulations having substrate adhesion and coating characteristics similar to those seen in solvent-based systems. Efforts were also directed toward development of aqueous intumescent coatings capable of imparting flame spread resistance when applied to wood substrates.

III. Program Outline and Experimental Approach

A general outline of the program of study is listed in Table II. In the initial stage of the project, studies were carried out to determine microsphere and aqueous binder compositions most suitable for use in irtumescent formulations.

The best binder and microsphere compositions from these studies were then used in advanced formulation development work to upgrade coating performance characteristics to the point where intumescent performance would be comparable with current solvent-based intumescent paints. This advanced work included studies of formulation modifiers and substrate surface treatments for improved intumescent coating appearance and performance.

TABLE II

OUTLINE OF CONTRACT R&D PROGRAM
FOR AQUEOUS INTUMESCENT COATINGS

I. CHARACTERIZATION AND SCREENING OF FORMULATION COMPONENTS

A. Preliminary Testing

B. Microsphere Composition Studies
   1. Polymerization Variables
   2. Thermal Characterization
   3. Performance in Halogenated Binder Systems

C. Binder Screening/Formulation Studies
   1. Variations in Binder Composition
   2. Variations in Microsphere/Binder Ratio

II. ADVANCED FORMULATION DEVELOPMENT

A. Microsphere Foaming Efficiency Studies

B. Screening of Formulation Additives
   1. Increased char-formation
   2. Improved flame-suppressant characteristics
   3. Brightness/Adhesion Modifiers
   4. Additives for Improved Coating Quality
   5. Substrate Primer Treatments

IV. Experimental Procedures

Experimental Procedures used in the course of the project are described in detail in Appendix VII A. For a better understanding of the experimental results in the section to follow, those experimental methods most commonly used in the present work are briefly discussed below.

Formulation

Saran microspheres were prepared by limited coalescence emulsion polymerization techniques which are described in patent literature[3]. For the present work, a wet cake of saran microspheres (65% solids aqueous) was used. For preparation of coatings, microspheres were added with stirring to aqueous latex dispersions, followed by other fillers and/or additives, when used. In the last step of coating makeup, thickeners were added to the formulations for proper coating rheology.

Substrate Application

Microsphere-latex formulations were applied to both wood and steel substrates. In the case of most wood coatings, a 36-mil coating bar was used to apply a coating thickness of about 36-mils wet to 1/4 inch marine plywood strips, 4" x 24". The coated strips were dried at room temperature for 4-5 days, leaving a final coating thickness of 8-10 mils.

For most steel substrate coatings, the same coating bar was used to apply coatings to 4" x 12", 24 gauge steel panels. Panels coated 36 mils wet had coating thickness of 8-10 mils after 4-5 days drying. Most of the experimental work was carried out with panels that were either cleaned or pretreated with zinc phosphate (Bonderite 37). For measurement of thermal insulation characteristics of the coatings, formulations were applied as described above to steel panels having thermocouples spot-welded to the center of the back sides of the panels. In certain instances, both wood and steel test panels were pretreated with primers and other coatings prior to application of intumescent formulations.

Flame Testing Methods

Intumescent coating performance, when tested on plywood panels, was measured by the two-foot flame spread tunnel test (ASTM E84), wherein the coated panel is inclined at a 28° angle over a closely-regulated flame source (Fisher burner). The progress of the flame up the face of the test panel is visually observed for a four-minute period, and the maximum distance which the flame travels up the panel is recorded. Using a standard reference chart, a flame spread rating is then determined for the test specimen, which correlates closely with results obtained in a 25-foot horizontal flame tunnel test.

Two types of flame testing were used in work with coated steel panels. For preliminary screening purposes, coated panels were placed on a ring stand, coated side down, 1 1/2" above the top of a Fisher burner. Samples

were exposed to the Fisher burner flame for 15 seconds. Panels were
then removed and examined for char thickness, density, and adhesion.
Better candidates from the 15-second flame test were then evaluated
by the 30-minute flame insulation test.

The 30-minute flame test procedure adapted for the present work corresponds
in some measure to ASTM E-119. Using an apparatus diagrammed in Figure 3,
steel panels coated as described above and having thermocouples spot-welded
to their uncoated sides were positioned 2.3 inches above a Fisher burner
fired with methane at 4 ounce pressure. The thermocouples were connected
to a millivolt strip chart recorder, and panel backside temperature was
continuously monitored for a testing period of 30 minutes. The primary
performance goal of the formulation work described in this report was
to develop aqueous coatings which, when applied to steel panels, could
provide sufficient insulation by intumescence to maintain panel backside
temperatures below 1,000°F (the approximate softening point of stressed
steel) for the duration of the test.

V. Experimental Results and Discussion

A. Characterization and Screening of Formulation Components

1. Initial Experiments

Initial work began with observations on the foaming characteristics of
microspheres through the addition of Experimental Resin XD-8217 to a
commercial acrylic interior house paint. Coatings modified in this

FIGURE 3

TESTING APPARATUS FOR 30-MINUTE
STEEL PANEL FLAME INSULATION TESTING
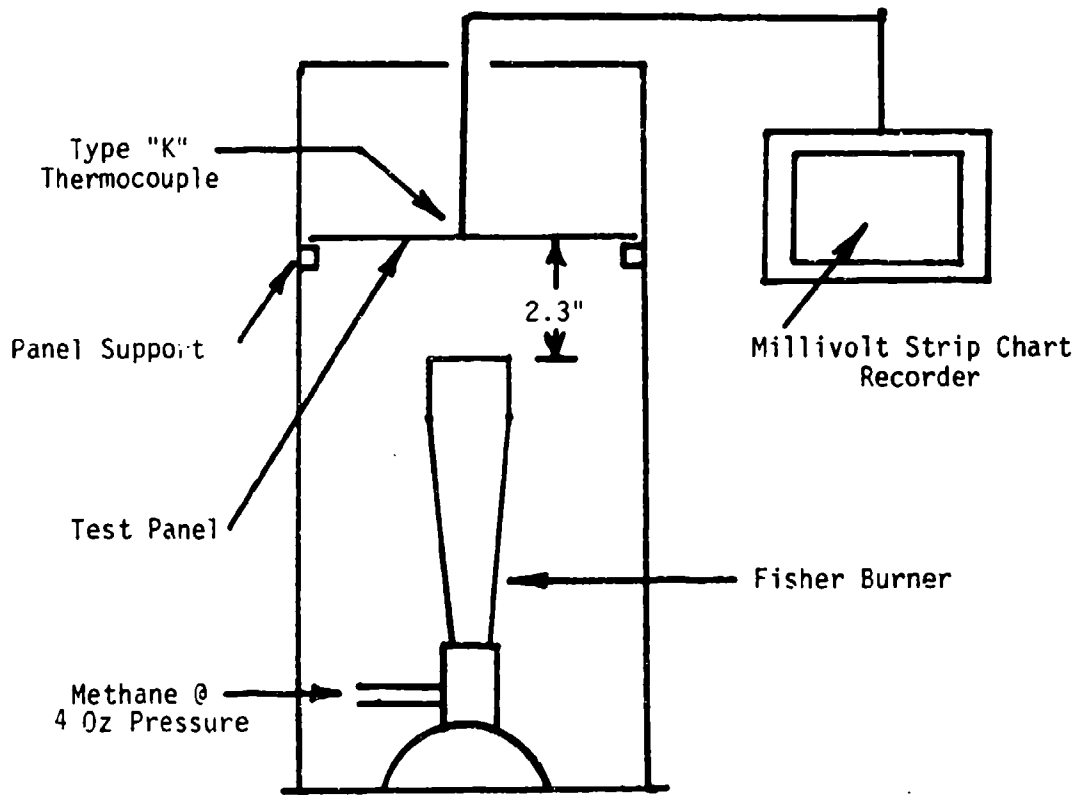
manner were applied to tongue depressor blades, dried at room temperature, and then briefly exposed to flame from a Bunsen burner. In this testing, it was noted that Stage I expansion occurred as expected, immediately after the specimens were subjected to heat. Stage II char formation did not occur, however, apparently due to the fact that (1) the microspheres melted and collapsed as heating continued, and (2) the acrylic polymer used as binder was not particularly well-suited for char formation.

In order to achieve desirable foaming and char-forming characteristics, a dual program was initiated. The first part consisted of a study wherein composition of the microsphere polymer was varied to obtain products having higher melting points so that Stage I foams would have better resistance to thermal collapse. The second part of the program, carried out concurrently, consisted of a screening study to identify binder systems having best char-forming characteristics.

2. Microsphere Composition

a. Microsphere Composition and Thermal Characteristics

Saran microspheres as currently manufactured are based on a vinylidene chloride-acrylonitrile composition. Among other components, divinyl-benzene is present in small quantities in the microsphere polymerization recipe as a polymer cross-linking agent to control rate and degree of expansion of the microspheres.

In Table III, glass transition temperature values are listed for a
number of homopolymers, including those based on monomers used in
preparation of saran microspheres. Since polymers having higher T_g
values ordinarily exhibit higher melting points, then it would follow
that increasing the melting point of microspheres ordinarily containing
approximately 25% acrylonitrile might best be achieved by increasing
the levels of this monomer in the polymerization recipe.

A series of polymerization reactions was subsequently carried out,
wherein the vinylidene chloride/acrylonitrile monomer ratio was varied.
A detailed discussion of procedures is included in the appendix
(Section VII B). In this series, microspheres were prepared having
acrylonitrile monomer contents varying from about 8% to about 80%.
As seen in Figure 4, collapse temperature of microspheres after expansion
increases substantially as a function of acrylonitrile content until
acrylonitrile level reaches about 60% of total polymer composition.
Increase in polymer melt point levels off as higher concentrations of
this monomer are used.

Candidate compositions were then selected from this study to formulate
intumescent coatings for further testing. In addition to polymer
collapse temperature, polymer foam density (prior to melt and collapse)
was considered to be an important criterion for selecting materials
for use in coating formulation work, since foam density reflects the
degree of foaming (i.e., height of foam produced in Stage I) when
coatings are subjected to heat. Certain compositions used in formulating

TABLE III

SELECTED MONOMERS AND GLASS TRANSITION TEMPERATURE

Monomer	$Tg,°K$
Styrene	368
Methyl Methacrylate	378
Acrylonitrile	403
Methacrylonitrile	393
t-Butyl Styrene	436
Vinylidene Chloride	256
N-Vinyl Pyrrolidone	448
Methyl Acrylate	276
Butyl Acrylate	217
Butadiene	188

FIGURE 4

MICROSPHERE COLLAPSE TEMPERATURE VS
ACRYLONITRILE/VINYLIDENE CHLORIDE RATIO
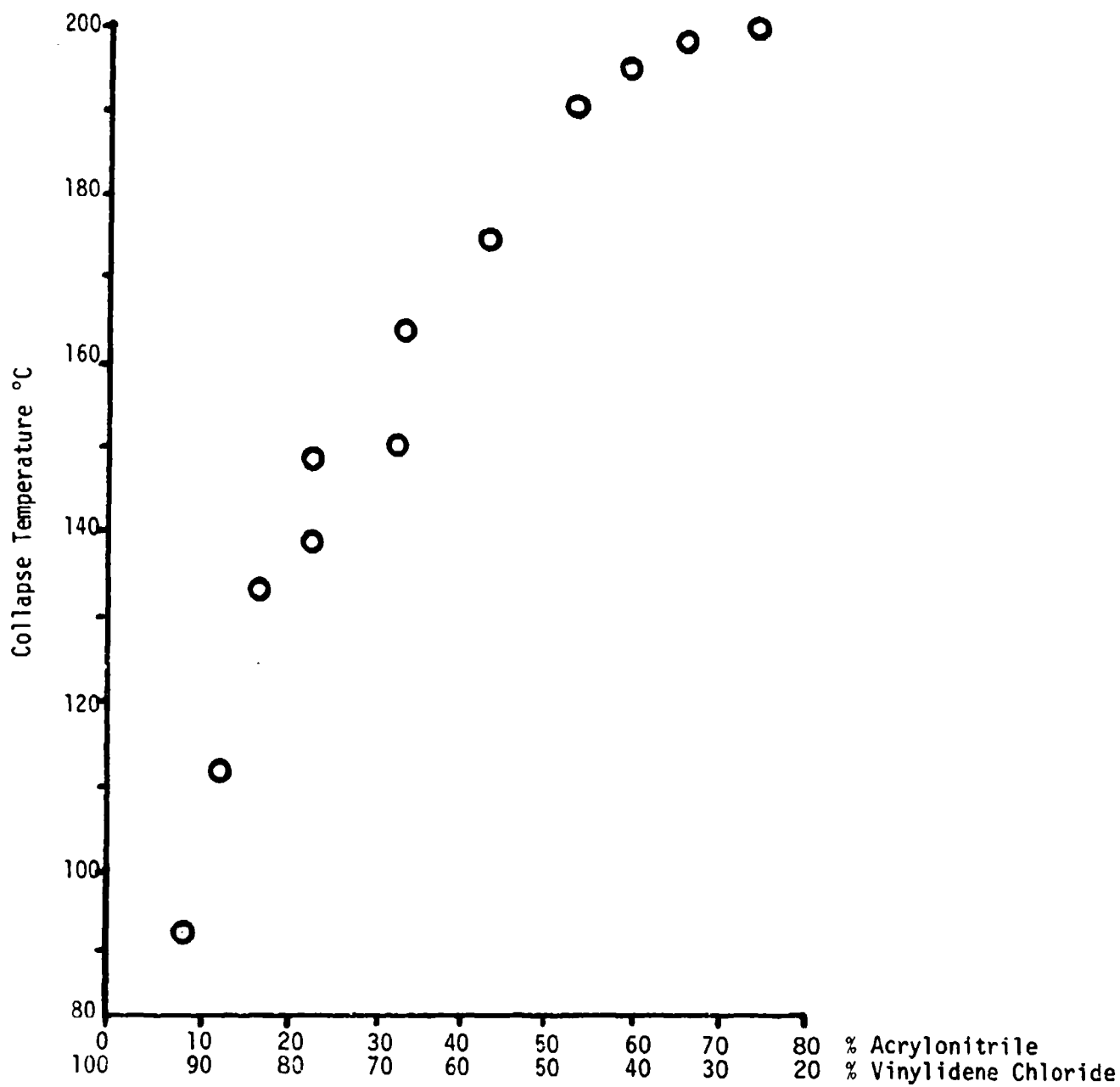
work employed blowing agents other than isobutane for better expansion
characteristics, particularly in compositions having higher acrylonitrile
content. Details on foam density and blowing agent are covered in
Appendix VII B. On the basis of foam density and thermal collapse
temperature measurements, a sample of high-acrylonitrile microspheres
designated SCP-42-82, containing approximately 54% acrylonitrile,
was chosen for further formulating work. For comparative purposes,
formulations were also prepared using commercial saran microspheres
(XD-8217) coutaining about 25% acrylonitrile.

Additional studies were carried out, wherein effects of other variations
in polymerization recipes on polymer foaming temperature, foam density, and
collapse temperature were measured. These studies included variations in
divinylbenzene cross-linker level, use of styrene monomer as a replacement
for vinylidene chloride, and use of compositions containing other experi-
mental monomers. On the basis of foaming and melt characteristics of
products prepared, however, none of these microspheres had foaming/melting
properties to warrant testing in intumescent coating formulations. These
studies are reviewed in detail in Appendix VII B.

b. Microsphere Composition and Intumescent Coating Performance

Formulation studies carried out concurrently with the polymerization
studies had shown Saran Latex 143 to be the binder of choice for
evaluation of the high-melting microsphere composition in intumescent
coatings. The following general formulation was used for evaluation:

Component	Formulation Level (Dry Basis)
Saran Latex SL-143	100 pts
Saran Microspheres	Varied
Igepal CO 630	1 pt
Alcogum 5950	0.5 pt

Using normal formulating procedures, compositions were prepared to contain
0, 10, 20, 30, and 40 parts microspheres per 100 parts latex. Compositions
were made up with Experimental Resin XD-8217 and with the higher-melting
SCP-42-82 microsphere product described above. Formulations were then
applied to steel panels for 30-minute flame testing. Coated at three
different wet coating thicknesses - 16, 32, and 42 mils. After air drying,
intumescent coating performance was tested via the flame insulation test
described previously, wherein coated panel insulative characteristics
are ordinarily tested over a 30-minute period. Determining differences
among coated panels described above, however, required that testing
be carried out for only 12-13 minutes. Results from these tests are
summarized in Table IV.

Data from Table IV shows no particular performance advantage using the
higher-melting microspheres. Indeed, if differences observed among
test specimens were considered to be significant, performance advantage
would appear to lie with use of standard XD-8217 microspheres. In
several cases, rapid increase in panel backside temperature was observed
during testing due to separation of the insulative char layer from the
panel. This type of failure was observed more frequently with compositions

TABLE IV

EFFECT OF MICROSPHERE COMPOSITION ON INTUMESCENT COATING PERFORMANCE: NORMAL-MELTING VS HIGHER MELTING MICROSPHERES

"A" Panels coated with compositions based on XD-8217 microspheres
"B" Panels coated with compositions based on SCP-42-82 higher melting microspheres

Panel Number	% MS In Binder	Coating Thickness (mils) Wet	Dry	Panel Flame Testing: Time (Min) to Reach 800°F	900°F	1000°F	Failure to Char
1	0	16	3	<1	<1	<1	---
2	0	32	8	<1	<2	<3	---
3	0	42	10	<1	<2	2.1	---
4A	10	16	3	<2	2.6	10.2	---
4B	10	16	3	<1	1.0	3.8	---
5A	10	32	7	2.7	8.9	>12	---
5B	10	32	7	1.8	5.2	5.6	5
6A	10	42	10	3.9	7.6	>12	---
6B	10	42	10	<2	3.3	7.5	9
7A	20	16	3	1	<2	<2	2
7B	20	16	3	<1	<1	2.0	---
8A	20	32	7	<2	2.8	>12	---
8B	20	32	7	1.1	1.9	<3	2
9A	20	42	11	--Thermocouple Failure --			
9B	20	42	11	2.0	4.0	10.0	10
10A	30	16	3	--Thermocouple Failure--			
10B	30	16	3	<1	<1	<1	<1

CONTINUED

TABLE IV CONTINUED

Panel Number	% MS In Binder	Coating Thickness (mils) Wet	Dry	Panel Flame Testing: Time (Min) to Reach 800°F	900°F	1000°F	Failure To Char
11A	30	32	8	--Thermocouple Failure--			
11B	30	32	8	<1	<1	<1	<1
12A	30	42	10	--Thermocouple Failure--			
12B	30	42	10	<2	2.5	6.0	---
13A	40	16	3	<1	1.3	5.0	---
13B	40	16	3	<1	<1	<1	<i
14A	40	32	7	<2	6.3	7.0	6
14B	40	32	7	1	<2	10	<1
15A	40	42	10	<2	<2	6.0	7
15B	40	42	10	<1	<2	<2	<1

TABLE V

MICROSPHERE ACRYLONITRILE CONTENT AND INTUMESCENT COATING PERFORMANCE

Formulation: Saran Latex 143   70 pbw (dry basis)
            Microspheres   30 " " "
            Thickener "L"   0.5 " " "

Coatings Applied 36 mils wet (8-10 mils dry)

MS Component	Acrylonitrile Content	Temperatures of Expansion	Temperatures of Melt/Collapse	Steel Panel Insulation Test-Time to 800°F	1000°F
XD-S217	~25%	90-95C	135-140°C	1.8 Min	5.5 Min
SCP-42-76-1	~64%	100-117°C	157-171°C	1.0 Min	1.8 Min

based on the high-acrylonitrile samples than with those based on the standard composition.

Further testing was then carried out comparing performance of the standard XD-8217 product with other microspheres having an even higher acrylonitrile content than SCP-42-82. Steel panel flame insulation characteristics were measured as above, with results summarized in Table V. As with experiments above, no advantage to use of higher-melting microspheres was demonstrated, and insulation characteristics of the standard XD-8217-based composition appeared to be somewhat better than that of the formulation containing a higher-melting microsphere product.

Otner studies were carried out wherein a non-flammable Freon compound was incorporated into microsphere polymerization recipes and used as a blowing agent, replacing normally-used isobutane. Surprisingly, use of this blowing agent did not have a significant effect on performance of microsphere-based intumescent coatings. This work was carried out in advanced formulation development studies, reviewed in a later section of this report.

c. Microsphere Composition - General Conclusions

Results from experiments above indicate that no performance advantage in intumescent coating formulations is gained using higher-melting microspheres, or at least not with those prepared with higher-than-normal levels of acrylonitrile in the polymerization recipe. Contrariwise,

there is some evidence for better intumescent coating performance using the standard, lower-melting microsphere product.

The polymerization studies of the present work were carried out primarily to upgrade thermophysical properties (i.e., resistance to thermal collapse) of microspheres for improved Stage I foam formation in the intumescent process. However, the thermochemical properites of the microsphere component in the formulation, and the ability of this component to release halogen for flame resistance and/or contribute to the total yield of carbonaceous material in Stage II char formation, could be considered of equal importance. Since both flame retardancy and char forming characteristics in polymer systems are tied closely to halogen content, it is speculated here that the performance advantage observed with the lower melting microsphere product may result from its higher halogen content, since XD-8217 has lower levels of acrylonitrile and higher levels of vinylidene chloride.

While it may be possible to arrive at microsphere compositions having both high resistance to thermal collapse and high halogen content through use of different comonomers or radically different polymerization techniques, time and expense would place such an endeavor beyond the scope of the present work. For this reason, subsequent work on the project was directed toward improving intumescent microsphere coating performance through formulation development work with standard XD-8217 microspheres, with primary emphasis on upgrading Stage II char formation characteristics.

3. Formulations, Screening and Optimization Studies

a. Initial Experiments

Concurrent with the microsphere polymerization studies, a program was initiated to identify binders suitable for use with microspheres in intumescent coatings, and to determine the levels of microspheres in formulations which provide the best performance in flame exposure conditions. In keeping with the original intent of the program, studies were carried out primarily with water-based halogenated polymer dispersions.

In an initial study, various combinations of microspheres and binders were prepared using procedures described previously and applied 30 mils wet to cleaned 24-gauge steel panels. After air-drying, panels were tested via the 15-second flame exposure test described earlier. Panels were also prepared and tested by exposing the back (uncoated) side of coated panels to determine coating behavior with application of backside heat.

Formulations used in the initial study and observations from flame testing are listed in Table VI. Included in the tests were panels coated with 30 mils (wet) of MIL-C-46081 intumescent paint.

These experiments were carried out to determine whether Saran Latex 143/Saran microsphere blends would show intumescence upon flame exposure, and to compare performance of such blends with a commercial intumescent paint. Saran Latex 143 was chosen as a binder because of its high halogen content

TABLE VI

PRELIMINARY FLAME EXPOSURE TESTING BY 15 SECOND PANEL TEST:
INTUMESCENT BEHAVIOR OF HALOGENATED LATEX/SARAN MICROSPHERE COMPOSITIONS
15 SECOND FLAME TEST RESULTS

Formulation Number	Composition[1]	Flame On Coated Side	Flame On Back Side
1	MIL-C-46081[2] Intumescent Paint	Stable Char, uneven, Maximum height 6 mm	No char, coating darkened and blistered
2	SL-143[3], 90 pbw[5] MS 10 pbw	Stable, heavy, continuous char. Maximum height 4 mm	Coating foamed, with moderate liftoff from panel
3	SL-143, 80 pbw MS 20 pbw	Same as #2, 4mm char	Foamed with severe liftoff from panel
4	SL-143, 60 pbw MS 40 pbw	Same as #2, 5 mm char	Same as #3
5	XD-8609.01, 90 pbw[6] MS 10 pbw	Coating carbonized, no char	Carbonized in area of maximum temperature
6	XD-8609.01, 80 pbw MS 20 pbw	Same as #5	Carbonized in immediate area of flame, with 2 mm MS foam ∿ 1" from center of panel
7	XD-8609.01 60 pbw MS 40 pbw	Same as #5	Same as #6
8	SL-143, 30 pbw XD-8609.01 30 pbw MS 40 pbw	Slight, spotty, discontinuous char	Coating liftoff similar to #3
9	#4 Applied to Panel Receiving double brush coat of XD-8609.01 as primer	Medium char, poor adhesion to substrate	Same as #3
10	XD-8155[7], 70 pbw MS 30 pbw	Stable, continuous char, somewhat lighter than with SL-143	Same as #3

[1] All MS/Latex formulations contained 0.5 pts Igepal CO630 dispersant & 3-5 pts Alcogum 5950 thickener.
[2] Ocean Chemical Company, mixed and applied per label directions.
[3] Saran Latex 143
[4] pbw = parts by weight, dry basis
[5] Saran Microspheres Experimental Resin XD-8217
[6] Experimental Latex XD-8609.01, Vinylidene/butadiene latex, 34% chloride, Dow Chemical
[7] Experimental Latex XD-8155, Saran latex, Dow Chemical

($\sim$60% chlorine), and its known ability to form a continuous film when dried at room temperature (many saran-type latexes require heat for proper film formation).

Observation of panels No. 2, 3, and 4 (Table VI) during flame testing showed that intumescence could indeed be obtained with saran latex/saran microsphere compositions as proposed earlier. In comparison with the solvent-based formulation (No. 1), the chars were more dense and of considerably greater strength (char from the commercial paint was fluffy, and could be blown away from the surface of the panel). The latex/micro-sphere coating, when heated, produced a char that reached a height of 4-5 mm above the panel surface; char from the commercial paint reached a height of 6 mm above the panel surface.

When panels coated with SL-143/XD-8217 formulations were heated on the back (uncoated) side, rapid foaming occurred, such that the latex film buckled and lifted from the panel surface. Char formation did not occur, since the foamed latex film did not have contact with the hot metal surface. When the commercial intumescent paint was tested in the same manner, the coating darkened and blistered, but did not intume ce.

Other compositions (No. 5-10) were prepared and tested in a similar fashion as listed in Table VI. Formulations 5-7 used a vinylidene chloride/butadiene latex binder. Latexes of this type generally have a lower chlorine content ($\sim$34%) than those of the saran family, but are recommended for use in applications where good adhesion is required.

As seen in Table VI, intumescence did not occur when coated panels were exposed to flame. Adhesion of the coatings to the steel substrate was far superior to that of the saran latex, however, particularly when panels were backside-heated. In an effort to obtain good char formation and improved hot adhesion, a 50/50 XD-8609.01/SL-143 blend was used in formulation No. 8. This did not prove successful, as the coating foamed but lifted off during backside heating, and char formation was substantially less than that obtained with SL-143 as the sole binder component. XD-8155 is a saran-type latex similar to SL-143, but is reported to have improved metal adhesion. When used with microspheres (formulation No. 10), resulting coatings formed char similar to SL-143, but no improvement was noted in resistance to lift off during backside heating.

b. Flame Spread Characteristics of Latex/Microsphere Compositions

For quantitative comparison of intumescent performance in latex/microsphere systems, the two-foot tunnel test described earlier was used to determine intumescent behavior for various compositions.

In the first series of tests, the effects of coating thickness and use of vinylidene chloride/butadiene latex primer were studied. Results are presented in Table VII. Using a 60/40 SL-143/XD-8217 composition, an improved flame spread rating was obtained at higher coating thickness (panels 1-3). A similar composition based on XD-8155 binder (panel 4) had a higher (worse) flame spread rating than the corresponding SL-143 formulation when applied at a wet coating thickness of 24 mils. At a 36-mil

TABLE VII
FLAME SPREAD RATINGS VIA 2 FOOT TUNNEL TESTING OF
SARAN MICROSPHERE/HALOGENATED LATEX FORMULATIONS
COATING THICKNESS AND WOOD PRIMER STUDY

PANEL/FORMULATION[1]	PRIMER[2]	FLAME SPREAD RATING
1. 40% MS in SL-143, 12 mils wet	No	40
2. 40% MS in SL-143, 24 mils wet	No	40
3. 40% MS in SL-143, 36 mils wet	No	36
4. 40% MS in Exp. Resin XD-8155, 24 mils wet	No	55
5. 40% MS in Exp. Resin XD-8155, 36 mils wet	No	31
6. 10% MS in SL-143, double brush coat, ∿ 2-3 mils dry	Yes	67
7. 40% MS in SL-143, 12 mils wet	Yes	53
8. 40% MS in SL-143, 24 mils wet	Yes	40
9. 40% MS in Exp. Resin XD-8155, 36 mils wet	Yes	36

[1]All formulations contained dispersant and Alcogum 5950 thickener as in steel panel test studies. Dry coating thicknesses were estimated at 4-6 mils when 12 mil wet coatings were applied, 6-8 mils dry for 24 mils wet, and 8-10 mils dry for 36 mils wet. Precise dry film thicknesses could not be measured due to irregular substrate thickness.

[2]Single brush coat of XD-8609.01 vinylidene/butadiene latex used as primer.

wet coating thickness (panel 5), however, the XD-8155-based composition showed a lower (improved) flame spread rating than a corresponding panel prepared in the same manner with SL-143 as binder. Panels 6-9 were primed with a single brush coat of XD-8609.01 vinylidene/butadiene latex. On primed panels, flame spread rating improved with increasing thickness of intumescent coating, but ratings were generally not as good as those observed in unprimed panels receiving the same type and thickness of intumescent coating.

Screening studies were continued to determine levels of microspheres and SL-143 binder affording best flame spread resistance. The 36-mil wet coatings of formulations prepared to have XD-8217 microsphere content ranging from 0-40% were applied to wood panels, dried, and tested via the two-foot tunnel. Results are listed in Table VIII and plotted in Figure 5. Also seen in Table VIII and Figure 5 are results from testing of panels coated with compositions based on microspheres containing Freon blowing agent and of panels coated with MIL-C-46081 solvent-based intumescent paint. In standard microsphere-based formulations, flame spread resistance improves as microsphere concentration increases, with little difference in performance between 20 and 40% microspheres in SL-143.

In observing the flame spread tests with compositions based on standard XD-8217-type microspheres, it was noted that considerable flashing (presumably of isobutane) occurred immediately upon exposure of the test panels to the flame. It was felt that release of isobutane (which accompanies microsphere expansion) and subsequent combustion of this

TABLE VIII

FLAME SPREAD RATINGS VIA 2 FOOT TUNNEL TESTING
OF SARAN MICROSPHERES/SL-143 LATEX FORMULATIONS

Formulation*	Flame Spread Rating	Char Characteristics
1. 40% XD-8217 in SL-143	36	Heavy surface char, little foaming
2. 20% XD-8217 in SL-143	38	Heavy surface char, little foaming
3. 10% XD-8217 in SL-143	48	Heavy surface char, very little foaming
4. SL-143, No MS	57	Surface char, very little foaming
5. 30% Freon MS in SL-143	67	Surface char, very little foaming
6. 60% Freon MS in SL-143	55	Surface char, very little foaming
7. MIL Spec Epoxy Intumescent Paint	21	Very thick, fluffy char. Excellent intumescence.

*Formulations contained Alcogum thickener and dispersant as described previously. MS/Latex coatings were applied 36 mils wet to 2' x 4" plywood test panels. The MIL spec coating was applied 17 mils wet. All coatings had thicknesses estimated at 8-10 mils when dry.

FIGURE 5

INTUMESCENT PERFORMANCE VS MICROSPHERE
CONCENTRATION IN SARAN LATEX 143 BINDER -
TWO FOOT TUNNEL FLAME SPREAD TEST
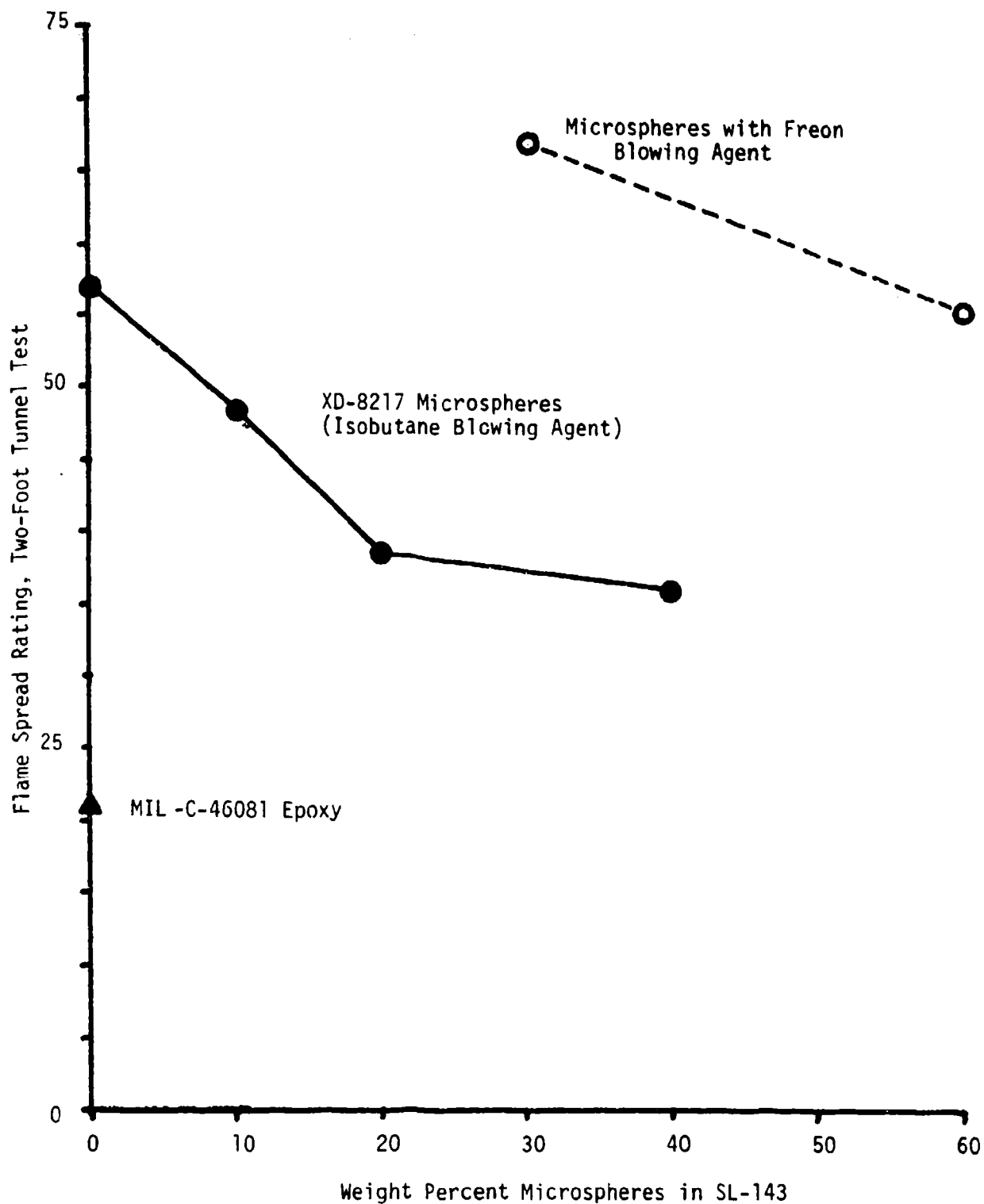
material in the immediate vicinity of the coating surface could result in binder and/or microsphere degradation, with poorer intumescent performance as a result. However, use of nonflammable Freon blowing agent in micro-spheres (formulations 5 and 6) did not improve flame spread resistance; performance was actually worse with this material.

For comparative purposes, a panel was coated with commercial intumescent epoxy formulation and tested (formulation 7). This material was superior to latex/microsphere formulations tested. Flame spread rating was better and degree of char formation was considerably higher than that observed with the aqueous latex/microsphere coatings.

c. Formulation Screening Via 30-Minute Panel Flame Tests

For thirty-minute steel panel flame insulation testing, SL-143/XD-8217 compositions were prepared wherein microsphere concentrations ranged from 0-40%. Formulations were applied at three different coating thicknesses: 16 mils wet (∿3 mils when dried), 32 mils wet (∿7 mils dry), and 42 mils wet (∿13 mils dry). Cleaned 24-gauge steel panels with thermocouples attached were used, and coated panels were tested for flame insulation characteristics as described previously. Results from these tests appear in Figures 6, 7, and 8. Data were not obtained for XD-8217-based compositions at the 30% microsphere level due to thermocouple failure; similar problems occurred with the test panel coated with 20% XD-8217 composition at the highest (11 mils dry) coating thickness.

FIGURE 6
PANEL FLAME TEST FOR XD-8217/SL-143 COMPOSITIONS

16 mil wet (3 mil dry) coatings

CF = Coating Failure Due to Char Separation

FIGURE 7
STEEL PANEL FLAME TEST FOR XD-8217/SL-143 COMPOSITIONS

32 mil Wet (7 mil Dry) Coatings

CF = Coating Failure due to char separation
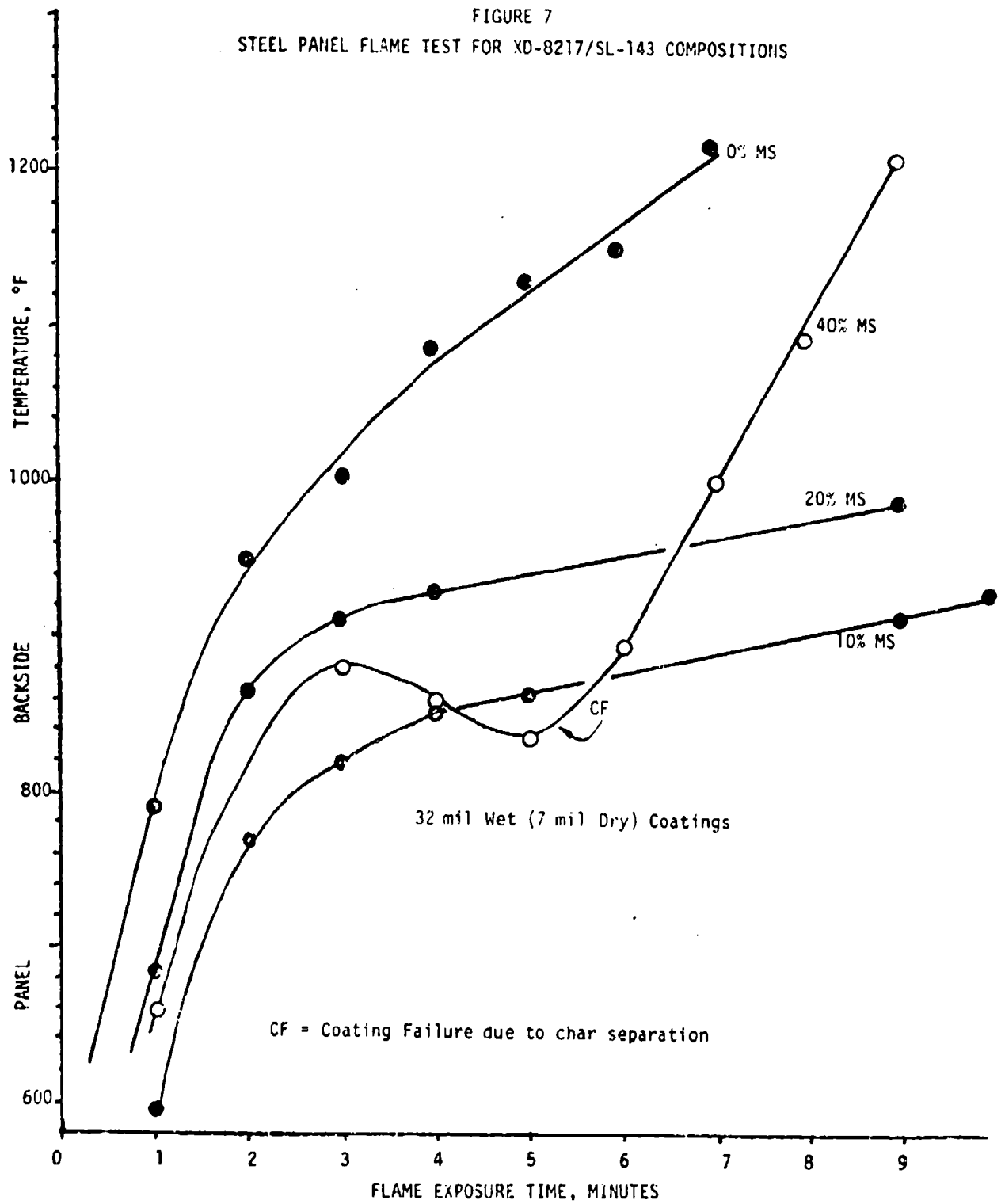
FIGURE 8
STEEL PANEL FLAME TEST FOR XD-9217/SL-143 COMPOSITIONS

CF = Coating Failure Due to Char Separation
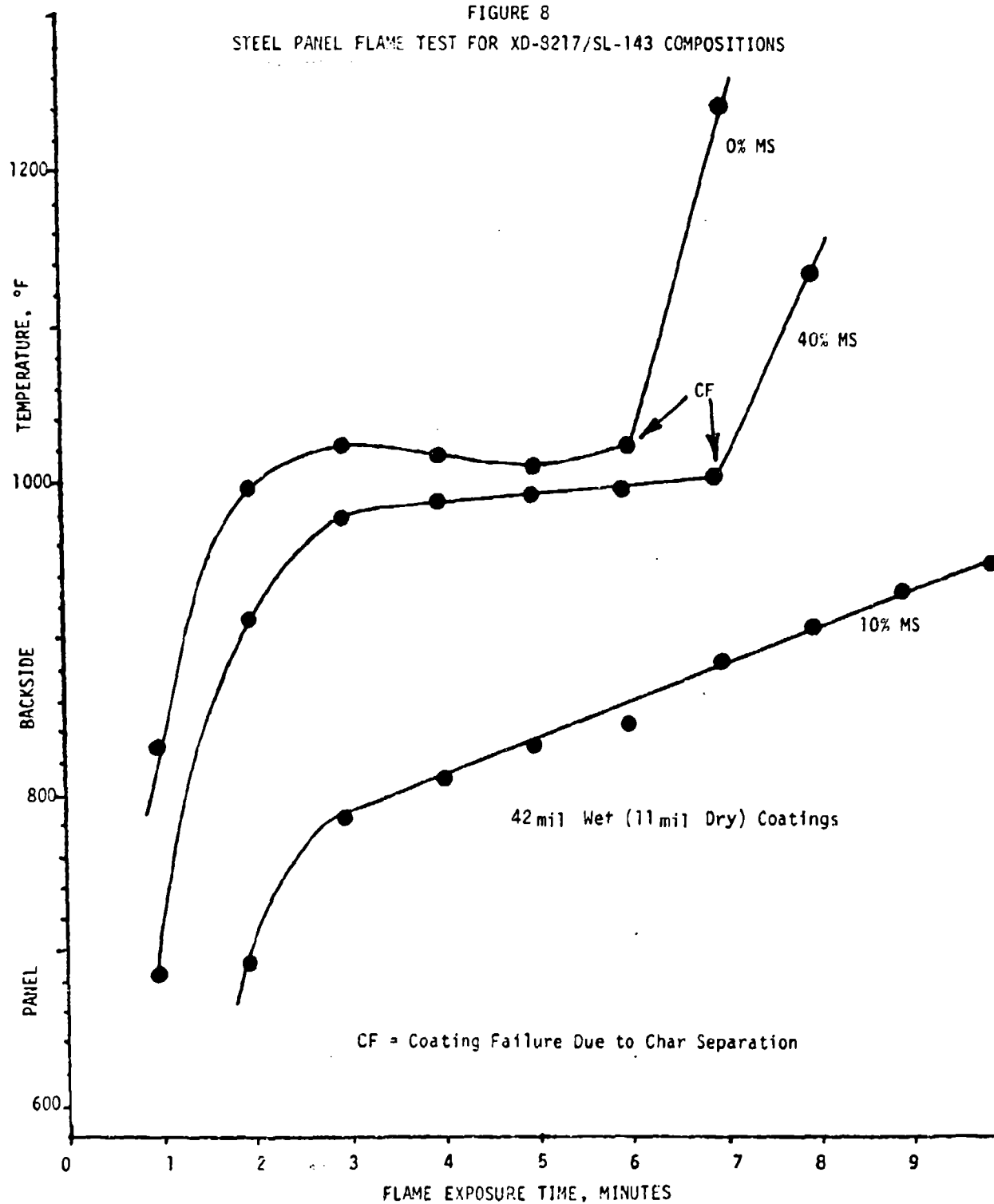
Results from these tests confirm that microsphere/latex coating compositions can provide flame insulation protection through a Stage I/Stage II intumescent process as originally proposed. Panel insulation test data indicate that (1) thermal protection generally increases as a function of coating thickness, and (2) better protection in this particular study was afforded at a 10% microsphere loading than at higher formulation levels.

One undesirable performance characteristic noted in many latex/microsphere compositions was first observed in these experiments. During flame testing, separation of the char from the steel substrate occurred with some of the test panels. When occurring, this "peeling off" of char from the panel would result in a rapid rise in panel backside temperature due to loss of char insulation protection. Coated panels exhibiting such behavior are identified in Figures 6-8.

For comparative purposes, a steel panel with thermocouple attached was coated with the MIL-C-46081 epoxy coating to give a film thickness of about 8 mils. Flame protection characteristics of the coated panel were measured by the 30-minute flame test, with results shown in Figure 9. On the basis of backside temperature rise, this solvent-based coating was superior to the latex-microsphere panels tested in the same manner as above. Panel backside temperature remained below 1,000°F over the 30-minute test period. While the char formed by the epoxy-based coating was of lower density and more fragile than the latex/microsphere formulations, separation of the char layer from the panel did not occur during the test.

FIGURE 9
STEEL PANEL TEST FOR MIL-C-46081 COATING
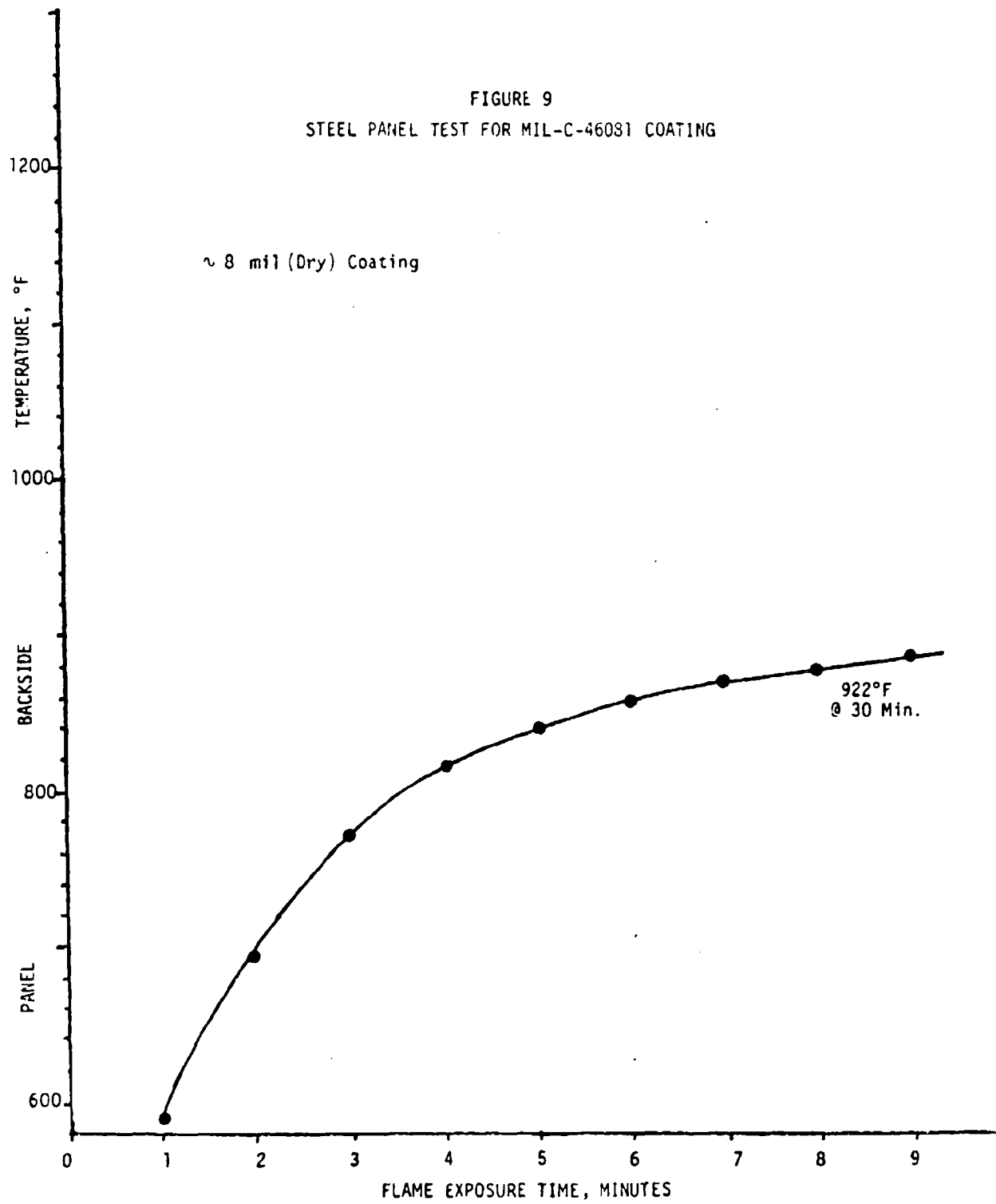
Variations in coating thickness and microsphere concentrations were then repeated using other binders. Using wet coating thicknesses of 16, 32, and 42 mils and the microsphere formulation levels of 10, 20, 30, and 40%, formulations were prepared, coated, and tested using XD-8609.01 vinylidene/ butadiene latex, SL-112 (a saran-type latex having a higher film-forming temperature than SL-143), and an aqueous epoxy binder system,

Results from panel flame insulation testing of the SL-112-based compositions are plotted in Figures 10, 11, and 12. As with SL-143-based formulations, coating insulation characteristics improved with coating thickness, and test failure due to char separation was observed more frequently in formulations containing higher microsphere levels. Although intumescent performance of compositions based on SL-112 could be considered similar to those based on SL-143, further work with SL-112 was not carried out due to very poor coating quality. The SL-112, with a higher T_g and higher minimum film formation temperature than SL-143, caused severe mud-cracking of film surfaces when used as the coating binder.

When panels coated with XD-8609.01-based formulations were tested in the same manner, a backside temperature of 1,000°F was reached within 2-3 minutes of testing, regardless of coating thickness and microsphere content. Char formation did not occur when these panels were subjected to flame exposure testing; instead, all of the films burned. Apparently, poor performance of this vinylidene/butadiene latex binder relative to SL-143 arises from its lower chlorine content.
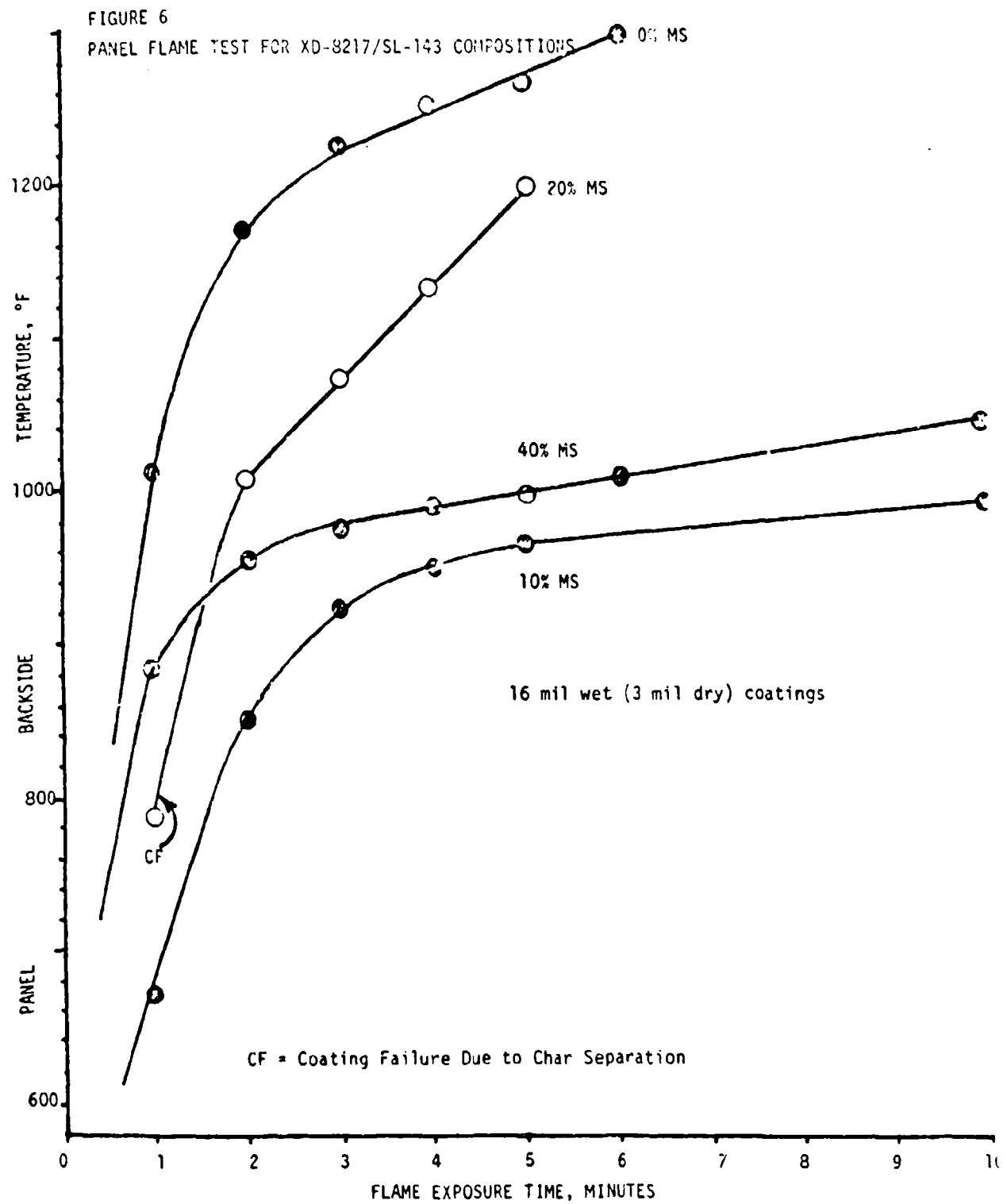
FIGURE 10
STEEL PANEL FLAME TEST FOR XD-8217/SL-112 COMPOSITIONS
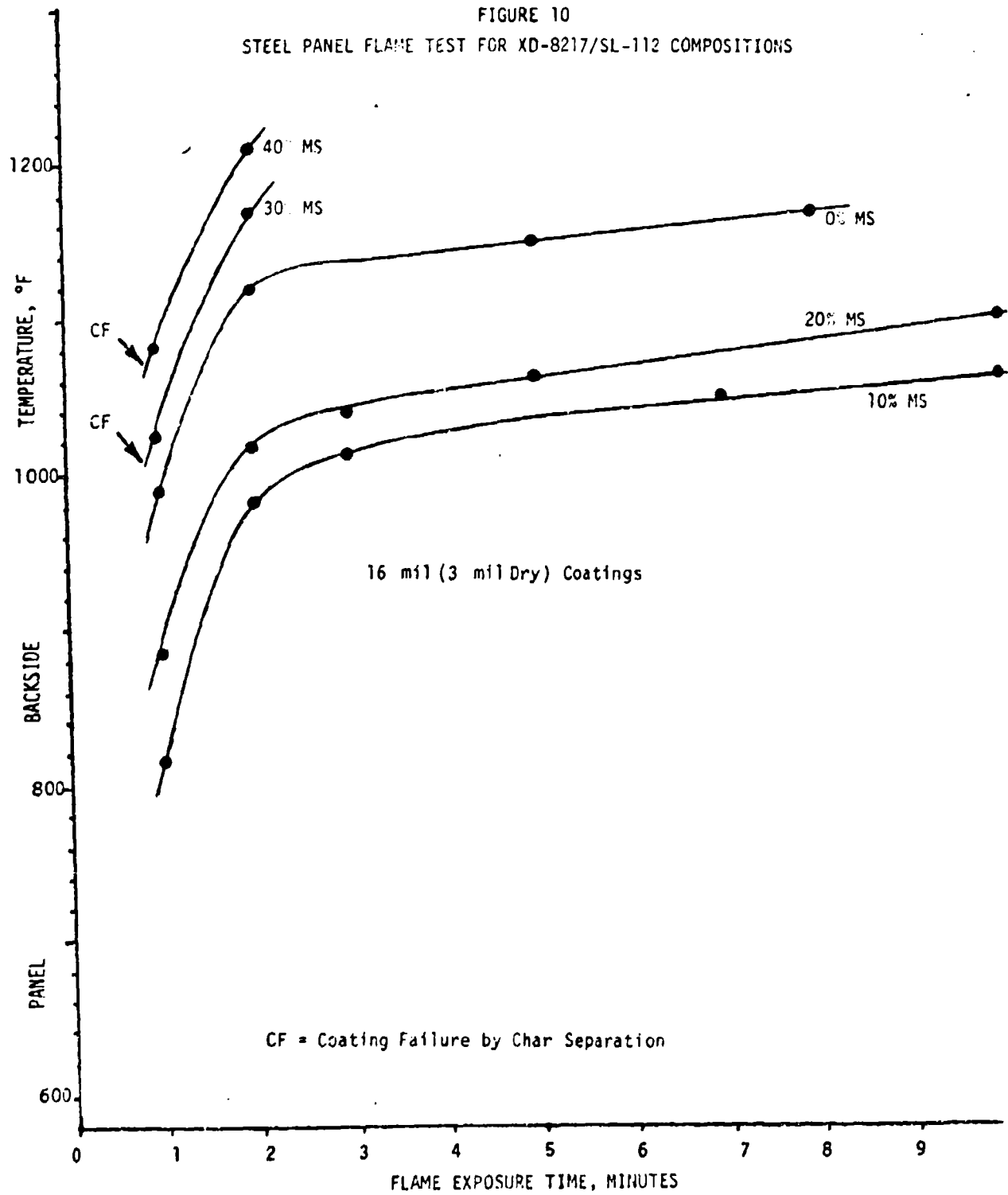
FIGURE 11
STEEL PANEL FLAME TEST FOR XD-8217/SL-112 COMPOSITIONS
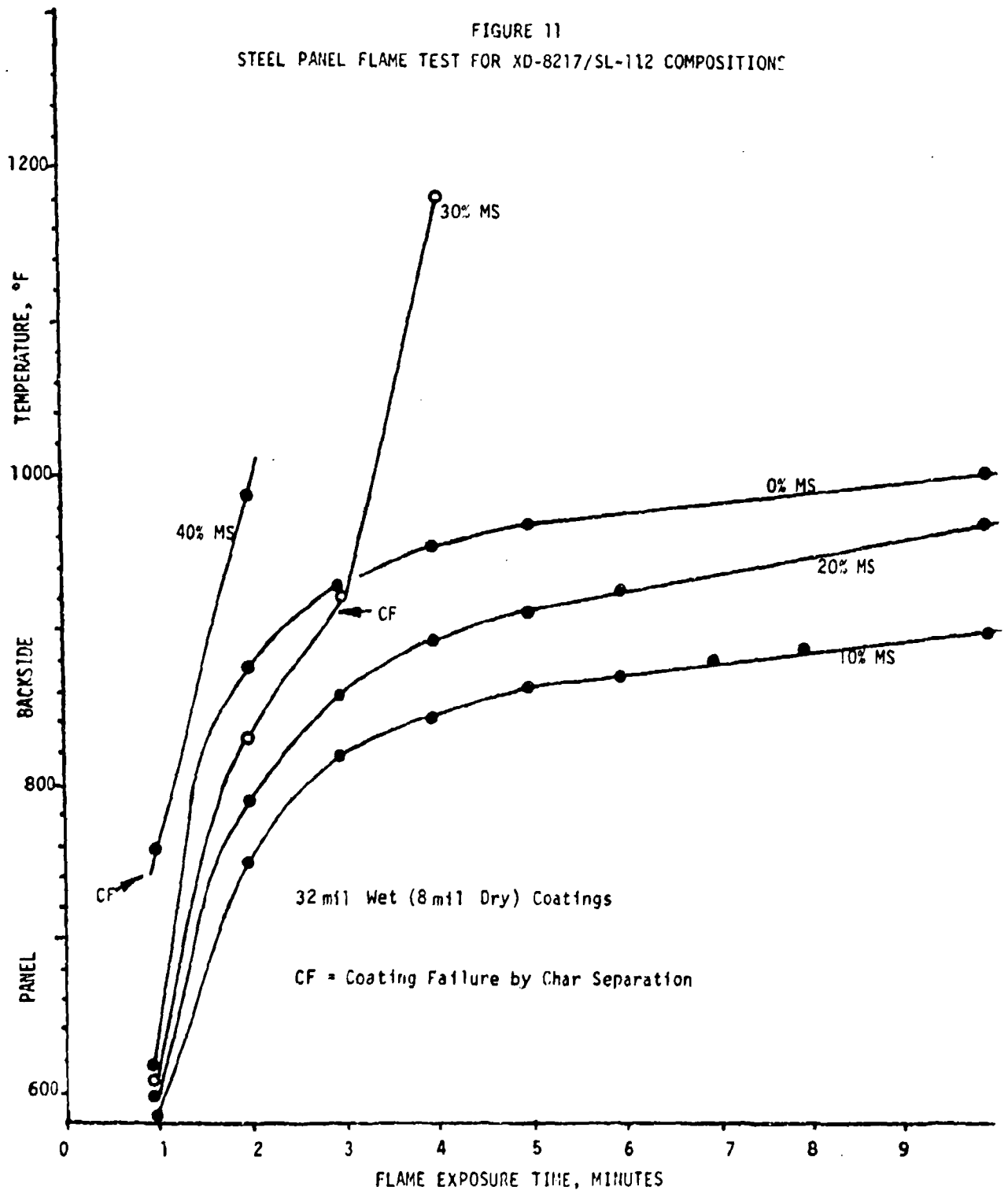
FIGURE 12
STEEL PANEL FLAME TEST FOR XD-8217/SL-112 COMPOSITIONS
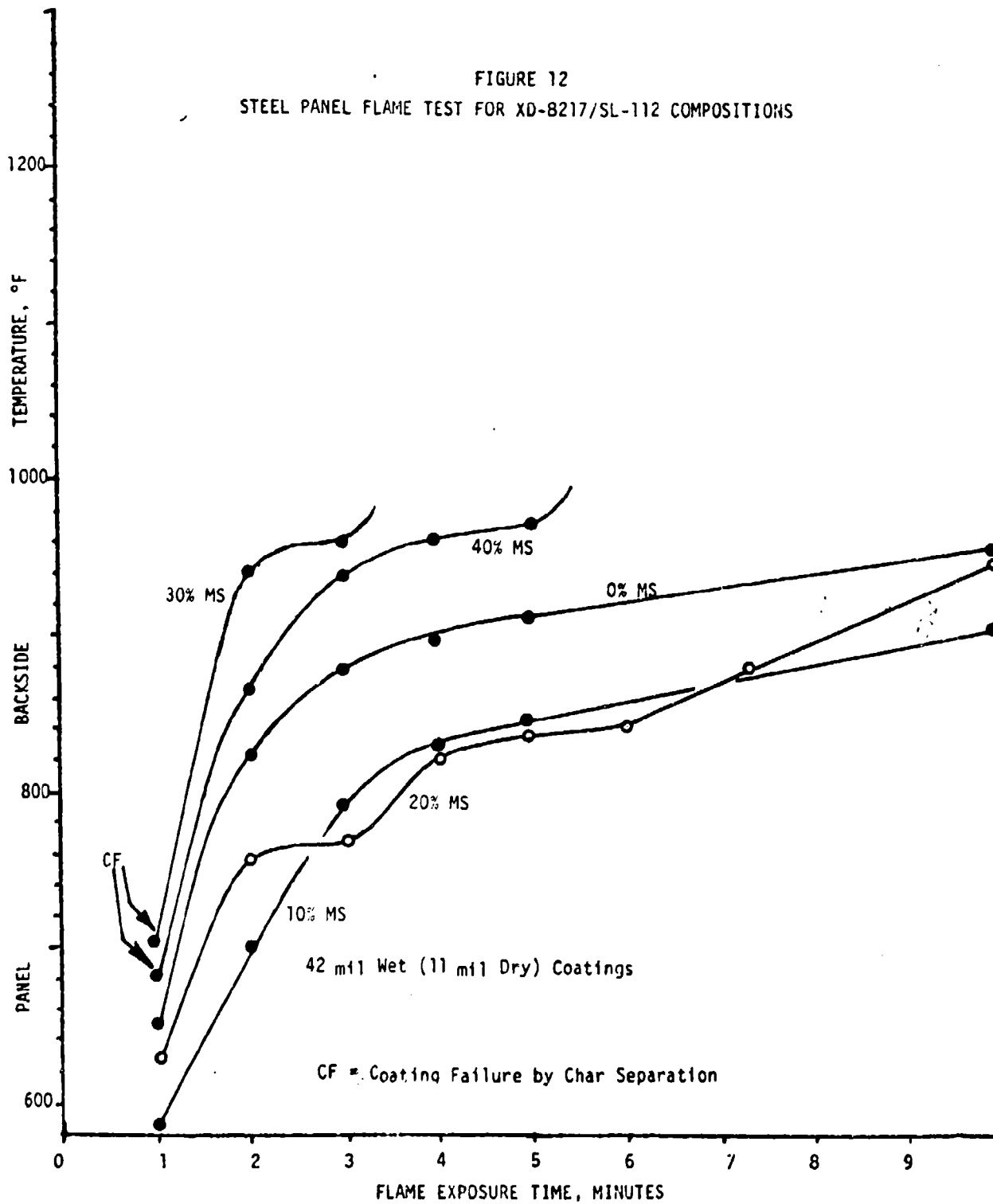
When panels coated with the aqueous brominated epoxy/XD-7080/microsphere compositions were tested in the same manner, intumescence did not occur, and backside temperatures rose rapidly to 1,000°F (within one minute). Foaming of the coatings did not occur upon flame contact. This was apparently due to either inability of microspheres to expand in a cross-linked resin matrix or poor thermal stability of the binder due to a relatively lower halogen content ($\sim$20% bromine).

Studies were then carried out to further observe intumescence during 30-minute flame tests using SL-143 binder. The following formulation

Saran Latex 143	80 pbw (dry)
XD-8217	20 pbw
Igepal CO 630	0.4 pbw
Alcogum 5950	5 pbw

was prepared and applied 32 mils wet to six steel panels. Results from 30-minute flame testing are seen in Table IX.

During flame testing, panels were observed closely to determine whether char separation occurred with flame exposure of char from the panels. Except for one panel, failure to provide insulation in each case occurred because of separation of char from the panel. From these tests, it was concluded that improved resistance of char peeling during flame testing should be a major goal of further work.

TABLE IX

THIRTY MINUTE FLAME TESTING OF STEEL
PANELS COATED WITH 80/20 SL-143/MICROSPHERE INTUMESCENT COATINGS

Panel Number	Coating Thickness (mils)	30-Minute Flame Test; Time to	
		1000°F (Min)	Char Separation (Min)
1	6.0	13.8	21
2	6.5	8.1	8.1-9.0
3	7.0	5.8	6.5
4	7.0	9.4	9.5
5	6.8	6.5	6.5
6	6.8	7.8	8.0

3. Conclusions From Formulation Screening and Testing Studies

At this stage in the program, a commercial saran microsphere product, XD-8217, appeared to be the material of choice for further development activities. Screening studies with microspheres having other copolymer compositions for higher melt/collapse resistance did not show any significant coating performance advantages. Use of a non-flammable Freon as a microsphere blowing agent similarly did not show an advantage over microspheres employing commonly-used isobutane for expansion.

Best all-around performance in binder screening work was shown by Saran Latex 143. Experimental Saran Latex XD-8155 showed no substantial advantage over SL-143 in flame spread testing. SL-112 showed similar intumescent performance to SL-143, but yielded films of poor quality. Foaming of microspheres did not occur during flame exposure when vinylidene/butadiene latex or water-dispersed brominated epoxy binders were used.

In flame spread testing of coated wood panels, formulations containing 20-40% microspheres exhibited best flame spread resistance. On metal panels, coatings containing 10% microspheres generally outperformed those having higher levels, where char separation frequently caused rapid loss of panel insulation. It was felt at this point, nevertheless, that higher microsphere contents could generate a higher degree of foaming and panel insulation, provided that the problem of char separation could be solved.

With regard to coating quality, saran latex/saran microsphere compositions exhibited good adhesion and appearance when applied to wood panels. Adhesion to metal panels (clean, untreated steel) was not considered to be satisfactory, however, and coating appearance was generally marginal due to yellowing and mud-cracking of the coating. It was felt that marginal adhesion and mud-cracking could be contributory to the relatively poor intumescent performance of aqueous microsphere/latex coatings on steel as compared to commercial solvent-based intumescent paints.

From these observations during the above screening studies, it was felt that advanced formulation development activities should be directed toward improved coating quality, improved char height and yield for better insulation, and improved resistance to char peeling (separation) during flame exposure.

B. Advanced Formulation Development Studies

Results from the screening/feasibility studies reported above indicated that intumescent coating performance is achieved in a two-stage foaming/char conversion process using saran microspheres dispersed in a halogenated latex binder. A water-borne formulation based on XD-8217 microspheres and Saran Latex 143 binder was found to impart short-term flame insulation protection to steel test panels, such that substrate backside temperatures remained below 1,000°F when exposed to flame. Such formulations, when applied to wood substrate, approach Class A performance in flame spread resistance.

With these simple latex/microsphere systems, however, deficiencies were noted when comparing performance with a solvent-based MIL-C-46081-type epoxy intumescent paint. The solvent-based paint provided adequate thermal protection for steel panels during 30-minute panel insulation testing (substrate backside temperature <1,000°F for more than 30 minutes), whereas aqueous microsphere systems provided adequate protection for only 10-12 minutes. When applied to wood substrate, the solvent-based paint gave a flame spread rating of 21, but a flame spread rating of 31 was obtained with the best latex/microsphere composition (a flame spread rating of <25 is required for Class A rating).

Visual observations of latex/microsphere coatings during and after flame exposure revealed a number of differences as compared to the solvent-based intumescent paint:

(1) Thickness of char layers generated by the aqueous microsphere/latex coating upon flame exposure was considerably less than that of the solvent-based system. However, char from the solvent-based paint was much more fragile and less durable than char from the aqueous coating.

(2) Failure of the aqueous-based coating on steel panels 5-13 minutes after onset of flame exposure occurred via separation (peeling) of the char layer from the test panels; this was not observed in testing of solvent-based paint.

(3) Steel substrate backside temperature remained lower upon flame exposure with solvent-based coating than with aqueous coating, even before char separation. The solvent-based system generates a lower-density char which apparently has a higher resistance to heat transfer.

(4) Flame exposure of the solvent-based paint results in uniform
surface coverage with char. In the aqueous system, however, char
formation is accompanied by cracking and contraction of the
surface coating, leaving a considerable portion of substrate exposed
directly to flame. This problem is more significant in coatings
applied to wood.

Based on these observations, a program of study was established to find
formulation modifiers which could upgrade thermal performance character-
istics of latex/microsphere compositions and also improve general coating
quality and appearance. Reported below are results from the following
experiments:

(1) Morphology study of latex/microsphere films for improved foaming/char
formation efficiency.

(2) Use of mineral fillers as additives for improved coating quality
and resistance to stress-cracking during flame exposure.

(3) Screening of plasticizer/coalescing aids for improved film formation
and foam expansion.

(4) Formulation additives for improved flame retardance.

(5) Additives for enhanced char formation.

(6) Advanced formulating studies using combinations of formulating
additives.

(7) Substrate treatments for improved coating quality and char adhesion.

1. Coating Morphology/Expansion Efficiency Studies

A series of laboratory tests was carried out to study factors affecting microsphere expansion efficiency and Stage I foam formation. Various latex/microsphere coating formulations were prepared, coated, dried and then expanded under controlled (275°F) conditions. Foam samples were then tested for degree of foaming and were examined by light microscopy. These studies, which are reviewed in detail in Appendix VII C, led to the following observations:

(a) Microspheres were well dispersed throughout the latex coating thickness. No problems with non-uniformity of microsphere distribution were seen.

(b) With 30% microspheres in the coating, free expansion of saran latex-based films will give a volume expansion of about 12-13 times. When kept oriented in "Z" direction expansion (i.e., when foamed while adhered to a substrate), volume increase is at best 3 to 3.5 times.

(c) Expansion in the "Z" direction orients the microsphere walls and voids in the expansion direction. They are no longer spherical.

(d) Voids caused by air bubbles, diffusion of isobutane or trapped
water will cause a fault or weak spot in the coating; degassing
formulations prior to application is a remedy.

(e) Thickener L (nonionic polyether thickener, GAF) and Elvanol
(polyvinyl alcohol, DuPont) appear to promote better expansion
than Alcogum 5950.

(f) Igepal CO-630 appears to plasticize formulations containing
Thickener L, but not formulations containing Alcogum. Microsphere
foaming efficiency is improved with addition of the plasticizer
to Thickener L.

A series of coatings was subsequently prepared to determine optimum
microsphere/latex formulation ratio and compositions using Thickener L
rather than Alcogum 5950 for coating rheology. Using the formulation:

Saran Latex 143 }	100 pbw dry basis with varied microsphere/
Microspheres (XD-8217) }	latex ratios.
Igepal CO-630	3 pbw
Thickener L	As required for proper rheology, 0.3-0.9 pbw

Coatings were applied 36 mils wet to wood panels, air dried to film thicknesses of 8-10 mils, and tested in the two-foot tunnel for flame spread resistance. Results from flame spread testing are seen in Table X. The formulation with a 70/30 latex/microsphere ratio provided best overall performance. Although formulations containing 60 and 80% microspheres yielded similar flame spread ratings, adhesion to panels was poor due to the higher concentrations of microsphere filler, and foamed coating separated from the wood panels during flame testing.

It was noted that flame spread ratings for the latex/microsphere compositions using Thickener L were somewhat higher (poorer) than those obtained when using Alcogum thickener (see Figure 3). This was studied further in repeat experiments by preparing separate 70/30 latex/microsphere coatings containing the two thickeners, coating (8 mils dry) on wood panels, and measuring flame spread via the two-foot tunnel test. The panel coated with formulation thickened with Alcogum 5950 (0.4 pbw) had a flame spread rating of 43, and panels coated with composition using Thickener L (0.6 pbw) had a flame spread rating of 52. Since this degree of variation in flame spread results is not uncommon in two-foot tunnel testing, these differences were not considered to be significant, and on the basis of foam expansion efficiency studies discussed above, Thickener L was chosen as the dispersant of choice for most of the formulation work remaining. It was observed in the work above that with use of either thickener, char formation upon flame exposure was only moderate as compared to the solvent-based paint, and

TABLE X

FLAME SPREAD PERFORMANCE OF LATEX/MICROSPHERE
COATINGS USING THICKENER L AS DISPERSANT

Latex/MS Ratio	Flame Spread Rating Two-Foot Tunnel Test
20/80 SL-143/MS	55
40/60 SL-143/MS	50
60/40 SL-143/MS	64
70/30 SL-143/MS	52

severe stress-cracking of the char and "checking" of the wood substrate occurred during flame testing.

2. Use of Mineral Filler Additives

Attempts at improving coating smoothness, reducing mud-cracking, and relieving char stress-cracking were made using mineral filler additives. Latex/microsphere compositions containing various levels of clay, calcium carbonate, and aluminum powder were prepared and coated on wood panels (8-10 mils dry) for flame spread testing. Steel panels were also coated (8 mils dry) with calcium carbonate-modified formulations for 30-minute panel flame insulation testing. Results from these tests are seen in Table XI. In comparing flame spread ratings of filled formulations with those of the control formulation containing no filler, it is seen that flame spread resistance was not improved with calcium carbonate and clay, and flame spread actually increased with the use of aluminum filler. While insulation performance was not improved with the use of clay, quality of the dried films appeared to be somewhat improved, and less char cracking was noted during flame spread testing.

3. Use of Plasticizers and Coalescing Aids

Preliminary formulation work using plasticizers for improved coating and char quality was begun using 100 parts (dry) of a 70/30 latex/MS blend modified with three parts (dry) Igepal CO 630 and nine parts (dry) Thickener L. These higher-than-normal formulation levels of dispersant and thickener were suggested from foam expansion efficiency studies

TABLE XI

INTUMESCENT COATING PERFORMANCE OF ALCOGUM-THICKENED
70/30 SARAN LATEX/SARAN MICROSPHERE FORMULATIONS CONTAINING FILLERS

Additive	Flame Spread Rating 2 Foot-Tunnel test, 10-mil Coating on Wood Panels	Steel Panel Flame Test Time To Reach	
		950°F	1000°F
None	36	--	--
$CaCO_3$, 5 phr	43	2.0	3.0
$CaCO_3$, 10 phr	45	1.7	1.8
$CaCO_3$, 20 phr	43	3.0	6.0
HT Clay, 10 phr	36	--	--
HT Clay, 20 phr	43	--	--
HT Clay, 30 phr	36	--	--
HT Clay, 50 phr	52	--	--
Aluminum Powder, 10 phr	50	--	--
Aluminum Powder, 20 phr	50	--	--

carried out previously. A wood panel coated with this composition gave a flame spread rating of 71 in two-foot tunnel testing (versus ~50 for formulations containing normal levels of dispersant and thickener). Observations during testing revealed that char formation was not enhanced with use of higher levels of these modifiers, and adhesion of coating to wood panels was poorer than normal.

Studies were also carried out using a 70/30 latex/MS blend modified with 5, 10, and 25% Santicizer 160 plasticizer (Monsanto). When these coatings were applied to steel panels and tested via 15-second flame exposure, there was no improvement in char formation over a standard 70/30 latex/ microsphere coated sample.

Other testing work was carried out using plasticizers and coalescing aids in conjunction with other formulation modifiers. Results from these studies appear in later sections of this report.

4. Formulation Additives for Improved Flame Retardance

Saran latex and saran microsphere products are both considered to have inherently good ignition-suppressant properties because of their high chlorine contents. Nevertheless, it was felt that investigations should be carried out to determine whether modification of latex/microsphere coatings with flame retardant additives could enhance coating performance in flame spread and panel insulation tests. Initial work was carried out using inorganic-type FR additives, using manufacturers' recommended

addition levels, based on chlorine content of 70/30 Saran Latex 143/XD-8217 blends. Additives chosen for this work were alumina trihydrate (added at 5, 10, and 20 parts per 100 parts coating), DuPont CM (a phosphate salt blend added at 5 and 10 parts), and colloidal antimony trioxide (Nyacol A-1550, Nyacol Chemical, added at 11.5 and 23 parts). Flame spread ratings were determined via two-foot tunnel testing of wood panels coated with each formulation (10 mils dry, 70/30 latex/MS ratio). Thirty-minute steel panel testing was also carried out with formulations modified with DuPont CM and alumina trihydrate. Results from these tests are listed in Table XII. As seen in the table, none of the FR additives improved the two-foot tunnel test performance over that seen with unmodified latex/ microsphere blends. Compared with unmodified blends tested previously, insulation performance on steel panels was likewise not improved with use of alumina trihydrate or CM phosphate additives.

Studies were then continued using halogenated organic flame retardant additives. Chosen for this work were FR-300 (decabromodiphenyl oxide, Dow Chemical) and FR-651 (penta-bromo-monochlorocyclohexane, Dow Chemical). Using FR-300, formulations were prepared according to the following recipe:

> SL-143 - 70 pbw (dry basis)
>
> XD-8217 - 30 pbw
>
> Thickener L - ~0.5 pbw
>
> Dow Corning Emulsion B - 4 pbw (wet)
>
> FR-300 - Varied, 10-50 pbw (dry)

Emulsion B defoamer was found necessary to avoid foaming during compounding.

TABLE XII

INTUMESCENT COATING PERFORMANCE OF ALCOGUM-THICKENED SARAN LATEX/SARAN MICROSPHERE FORMULATIONS CONTAINING FLAME RETARDANT ADDITIVES

FR Additive	Flame Spread Rating 2 Foot Tunnel, 10-mil Coated Wood Panels	Steel Panel Flame Test (10 mil coatings) Time To Reach	
		950°F	1000°F
None	36	--	--
Alumina trihydrate, 5 phr	43	1.5 Min	1.6 Min
Alumina trihydrate, 10 phr	36	1.5	1.6
Alumina trihydrate, 20 phr	36	1.5	1.6
DuPont CM, 5 phr	43	--	1.7
DuPont CM, 10 phr	40	--	3
Nyacol Sb_2O_3, 11.5 phr	36	--	--
Nyacol Sb_2O_3, 23 phr	45	--	--

The formulation used in preparing FR-651-modified compositions is given below:

        SL-143 - 70 pbw (dry basis)

        XD-8217 - 30 pbw

        DOWFAX 2A0 - 2 pbw

        Nopco Defoamer - 2 pbw

        Alcogum 5950 - 1.25 pbw

        FR-651 - Varied, 10-30 pbw

The use of DOWFAX 2A0 (plasticizer/dispersant, Dow Chemical) and another defoamer (Nopco) were required to promote the formation of a smooth, well-dispersed coating when using FR-651 additive.

Formulations were applied to wood test panels (8 mils dry) for flame spread testing. Flame spread was also measured for a standard 70/30/0.5 SL-143/XD-8217/Thickener L composition for comparative purposes. Steel panels were coated with compositions prepared above containing 30 pbw FR-300, 30 pbw FR-651, and the unmodified standard formulation. Results from flame spread testing are listed in Table XIII. Results from 30-minute steel panel testing are seen in Figure 13.

As seen in Table XIII, use of FR-300 and FR-651 led to substantial improvements in flame spread resistance when either additive was used at 10-30 pbw levels. Figure 13 shows that a very substantial improvement in steel panel insulation protection is obtained with use of 30 parts FR-300 as modifier for the latex/microsphere coating. Although failure

TABLE XIII

EFFECT OF HALOGENATED FR ADDITIVES
ON FLAME SPREAD RESISTANCE OF
70/30 LATEX/MICROSPHERE COATINGS APPLIED TO WOOD PANELS

Formulation*	Flame Spread Rating, Two-Foot Tunnel Test
70 pts SL-143 (dry basis) + 30 pts XD-8217	
No additive	59
+ 10 pts FR-300	43
+ 20 pts FR-300	43
+ 30 pts FR-300	40
+ 50 pts FR-300	64
+ 10 pts FR-651	43
+ 20 pts FR-651	43
+ 30 pts FR-651	43

FIGURE 13

INTUMESCENT PERFORMANCE OF LATEX/MICROSPHERE COMPOSITIONS CONTAINING FLAME RETARDANT ADDITIVES

CF = Coating Failure Due to Char Separation
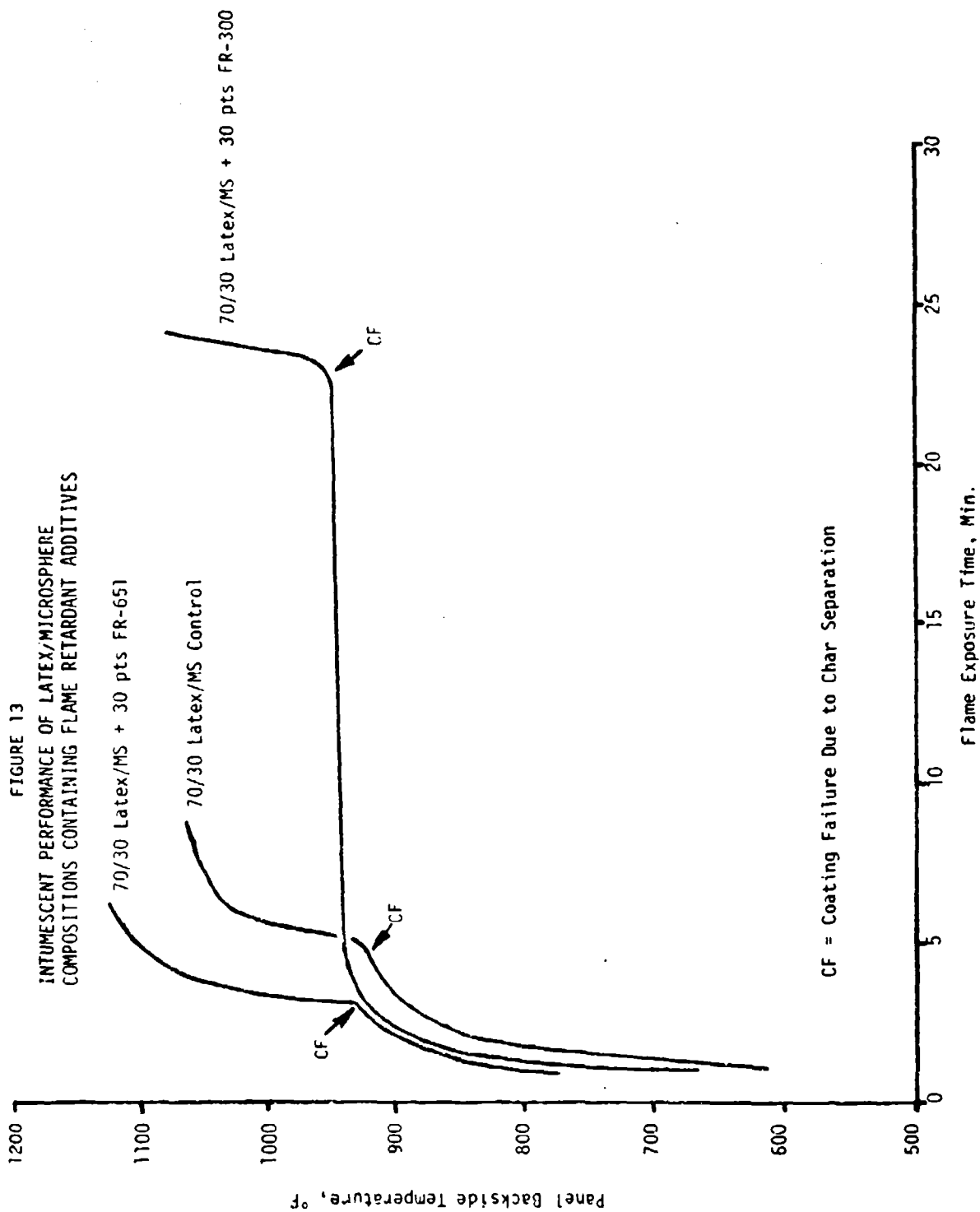
by means of char separation occurred with all three panels tested, time
to char failure with the FR-300-modified system was prolonged to about
25 minutes. Steel panels were then prepared by coating 70/30 blend as
above, but including 10 parts and 50 parts FR-300. Results from 30-minute
steel panel testing are plotted in Figure 14. Although insulation
performance was somewhat less than that of compositions containing 30 parts
FR-300, both coatings provided insulation without char failure over the
duration of the test. With all coatings containing FR-300, char adhesion
was considerably better than that of unmodified control formulation.
Mud-cracking, which occurred as the formulations dried on both wood and
steel substrates, was evident in all compounds containing either one
of the organic flame retardant additives.

Performance of these compositions represented the first instance in
this development program wherein intumescent behavior of an aqueous
latex/microsphere coating approached that of the solvent-based MIL-C-46081
epoxy coating.

5. Additives for Increased Char Formation

Two approaches were used in this study. To determine whether addition
of particulate carbon could increase carbon char levels during flame
exposure, the standard latex microsphere composition (using Thickener L
as the dispersant) was modified with carbon black at two levels (5 parts
and 10 parts per 100 parts of dry coating solids). Wood panels were
coated (36 mils wet) in the usual manner, and flame spread resistance was

FIGURE 14

INTUMESCENT PERFORMANCE 70/30 LATEX-MICROSPHERE COMPOSITIONS
MODIFIED WITH FR-300

50 pbw FR-300

20 pbw FR-300

Flame Exposure Time, Min.

Panel Backside Temperature, °F
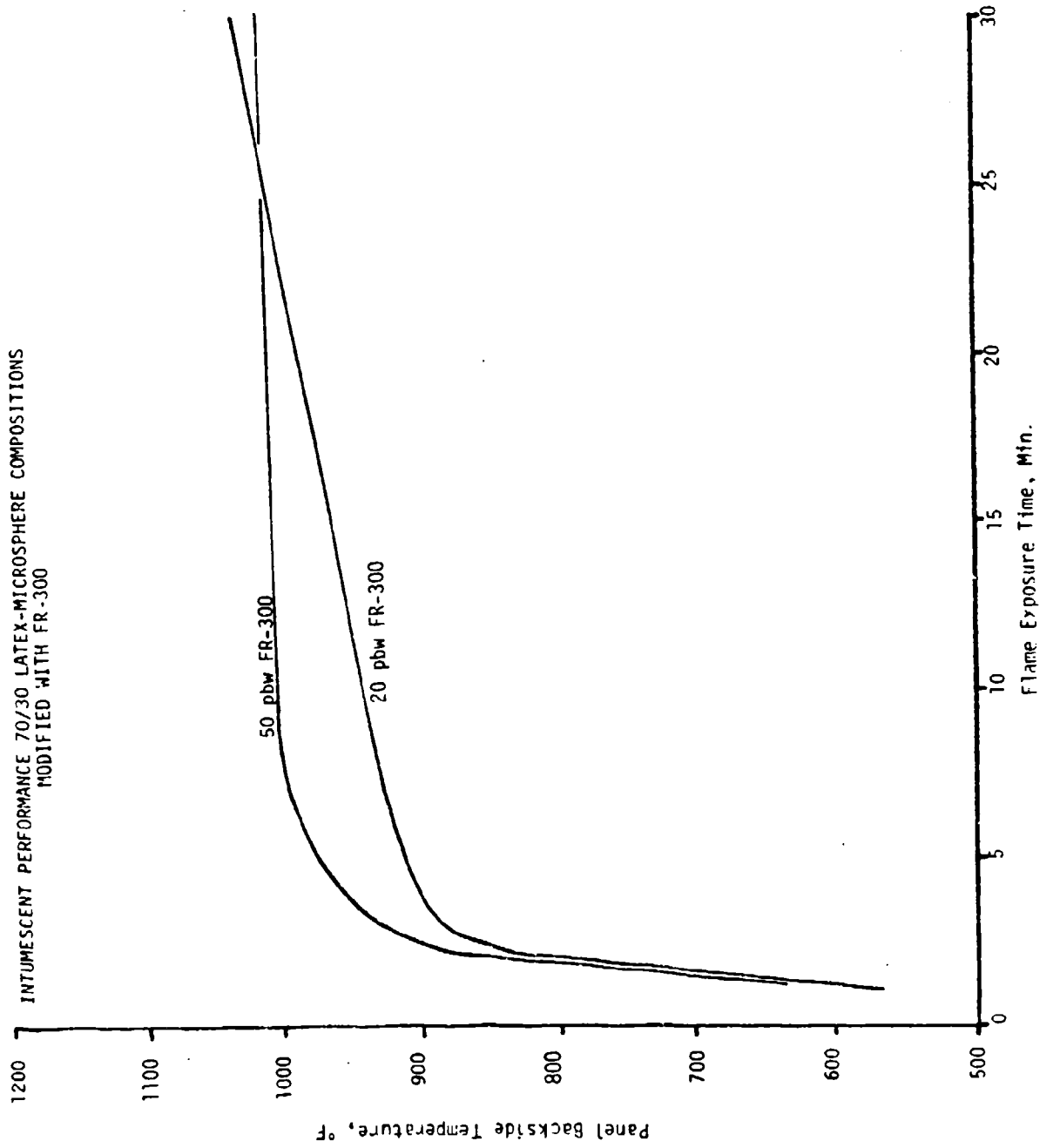
measured. In the second approach, a particulate plastic filler was used.
This material, designated in this report as B-1550 resin, is an experimental
saran-type polymer from Dow Chemical, having a high chlorine content. The
material was added as a micronized powder. Since many saran polymers form
a char upon heating, it was believed that addition of this filler might
enhance char formation of latex/microsphere coatings during flame exposure.
Using the standard 70/30 recipe with Thickener L, but modified with 50 parts
B-1550 resin, 36 mil wet coatings were applied to wood panels and dried.
Results from flame spread testing of carbon-filled and B-1550-filled coatings
are listed in Table XIV.

As seen in the table, use of carbon black filler led to poorer resistance
to flame spread. With use of the B-1550 resin as a formulation additive,
however, flame spread resistance of the latex/microsphere coating was
improved substantially. Visual observation of panels after flame testing
showed that use of this polymeric additive resulted in an increased level
of char formation during flame exposure.

6. Advanced Formulating Studies

Screening studies had identified FR-300 and B-1550 resin as additives which
could upgrade thermal performance characteristics of latex/microsphere
blends. Advanced formulation development was then continued with modifica-
tion of standard 70/30 0.5 latex/microsphere/Thickener L compositions using
these and other additives. In Table XV, results are listed from testing
of 23 formulations wherein types and levels of formulation modifiers were
varied in order to improve coating quality and char forming characteristics.

TABLE XIV

EFFECT OF CARBON AND MICRONIZED SARAN
PLASTIC FILLERS ON FLAME SPREAD RESISTANCE OF
LATEX/MICROSPHERE COATINGS

Formulation	Flame Spread Rating, Two-Foot Tunnel
70 pbw SL-143 30 pbw XD-8217 $\sim$ 0.5 pbw Thickener L	
No Additive	52
+ 5 pbw carbon black	81
+ 10 pbw carbon black	64
+ 50 pbw B-1550 resin	36

TABLE XV -- Part 1. INTUMESCENT COATING PERFORMANCE OF MODIFIED MICROSPHERES-LATEX COATINGS

Standard Formulation: 70 Parts Saran Latex SL-143 + 30 parts Saran Microspheres XD-8217, Igepal CG-630 as MS dispersant, GAF Thickener L for coating rheology. 36 mil wet films applied to plywood panels for flame spread and steel panels for panel flame testing.

Formulation Number	Modification	Flame Spread Rating, Two-Foot Tunnel Test	Steel Panel Flame Test. Time to 100°F on Backside (Min).	Remarks
1	None-Control	52	5.5	Low char, with large cracks after flame exposure.
2	10 pts FR-300	43	22.0	Decabromodiphenyl oxide. Improved char adhesion noted.
3	30 pts FR-300	40	24.8	Better char adhesion than control.
4	50 pts FR-300	64	9.8	Better char adhesion than control.
5	50 pts B-1550 Resin	36	3.0	Particulate Saran Resin filler. Cracks in coating. Higher char yield than control.
6	30 pts B-1550 + 5 pts Hercolyn D	38	----	Thicker char than control on wood and steel, better coating appearance.
7	20 pts B-1550 + 10 pts Hercolyn D + 10 pts HT Clay	29	----	Better coating quality (fewer cracks), less char cracking. Higher char than control, but less than #6.

TABLE XV -- Part 2. INTUMESCENT COATING PERFORMANCE OF MODIFIED MICROSPHERES-LATEX COATINGS

Standard Formulation: 70 Parts Saran Latex SL-143 + 30 parts Saran Microspheres XD-8217, Igepal CO-630 as MS dispersant, GAF Thickener L for coating rheology. 36 mil wet films applied to plywood panels for flame spread and steel panels for panel flame testing.

Formulation Number	Modification	Flame Spread Rating, Two-Foot Tunnel Test	Steel Panel Flame Test. Time to 100°F on Backside (min).	Remarks
8	50 pts B-1550 Resin + 5 pts Hercolyn D Plasticizer	38	2.3	Higher char yield, but void space beneath char surface. Cracks in dry coating.
9	50 pts B-1550 + 10 pts Hercolyn D + 10 pts HT Clay	26	3.0	Better appearance of dry film, less cracking. Void space beneath char surface during panel flame testing.
10	50 pts B-1550 + 10 pts Hercolyn D + 10 pts HT Clay + 30 pts TiO$_2$	29	1.7	Better appearance of dry film, lighter color. Void spaces beneath char.
11	50 pts B-1550 + 10 pts Hercolyn D + 3 pts Cab-o-Sil	--	2.5	Less cracking of coating. Void spaces under char.
12	50 pts B-1550 + 10 pts Hercolyn D + 3 pts Cab-o-Sil + 4 pts DOWFAX 2AO	26	---	DOWFAX added to give better dispersion. Little effect on appearance, performance. Void space beneath char surface.
13	50 pts B-1550 + 10 pts Hercolyn D + 3 pts Cab-o-Sil + 4 pts DOWFAX 2AO + 5 pts DALPAD A	26	---	DALPAD added to further reduce coating cracking. Poor coating adhesion.

TABLE XV -- Part 3.   INTUMESCENT COATING PERFORMANCE OF MODIFIED MICROSPHERES-LATEX COATINGS

Standard Formulation: 70 Parts Saran Latex SL-143 + 30 parts Saran Microspheres XD-8217, Igepal CO-630 as MS dispersant, GAF Thickener L for coating rheology. 36 mil wet films applied to plywood panels for flame spread and steel panels for panel flame testing.

Formulation Number	Modification	Flame Spread Rating, Two-Foot Tunnel Test	Steel Panel Flame Test. Time to 100°F on Backside (Min).	Remarks
14	70 pts XD-8609.01 replacing SL-143. 50 pts B-1550 + 10 pts Hercolyn D + 4 pts DOWFAX 2A0	64	1.0	Much lower char yield.
15	30 pts FR-300 + 10 pts B-1550	50	3.2	Similar to control on wood, better char adhesion to steel than control in 15 sec steel panel flame exposure.
16	30 pts FR-300 + 30 pts B-1550	29	16.0	Moderate char on wood, good char adhesion on steel.
17	30 pts FR-300 + 50 pts B-1550	29	12.0	Moderate char on wood, good char adhesion on steel.
18	30 pts FR-300 + 50 pts B-1550 + 5 pts Hercolyn D + 4 pts DOWFAX 2A0	31	4.1	Moderate char on wood, less dense char with void spaces on steel.
19	30 pts FR-300 + 50 pts B-1550 + 4 pts DOWFAX 2A0 + 3 pts Cat-o-Sil	29	1.6	Less coating cracking on coating applied to untreated steel panels.

TABLE XV, PART 4

INTUMESCENT PERFORMANCE OF SARAN LATEX/SARAN MICROSPHERE
COMPOSITIONS CONTAINING POWDERED MICA AS FILLER

Standard Formulation: 70 Parts Saran Latex SL-143 + 30 parts Saran Microspheres
XD-8217, Igepal CO-630 as MS dispersant, GAF Thickener L
for coating rheology. 36 mil wet films applied to plywood
panels for flame spread and steel panels for panel flame
testing.

Formu-lation Number	Composition	Flame Spread, Two-Foot Tunnel	Steel Panel Test, Time to 1000°F	Comments
20	70/30 SL-143/MS + 30 pts mica	43	1.7 min	Low char, very little stress cracking. Good adhesion to both wood and steel panels.
21	70/30 SL-143/MS + 30 pts mica + 30 pts FR-300	55	1.2 min	Similar to #20, but reduced adhesion to steel.
22	70/30 SL-143/MS + 30 pts mica + 30 pts FR-300 + 30 pts B-1550	43	2.0 min	Similar to #21.
23	70/30 SL-143 + 30 pts mica + 30 pts FR-300 + 30 pts TiO_2	43	1.0 min	Similar to #21, but improved coating brightness.

Laboratory studies had indicated some qualitative improvement in char formation with use of Hercolyn D plasticizer (Hercules). When used in combination with clay, Cab-O-Sil (Cabot), and TiO_2 fillers, some reduction in mud-cracking of dry coatings was noted, and use of TiO_2 improved coating brightness considerably. Most of the Hercolyn-modified formulations showed excellent flame spread resistance (flame spread ratings as low as 26 in formulations 9, 12, and 13). However, considerable void space (more-so than the control) after flame exposure was noted beneath the char surface of coatings containing Hercolyn plasticizer, whether applied to wood or steel substrates. Apparently due to this void space, insulation performance on steel panels was poor. Certain coatings containing Hercolyn D were also modified with DALPAD A and DOWFAX 2AO plasticizer (Dow Chemical) for improved coating quality (formulations 12, 13, 18, and 19). While flame spread resistance was excellent, mud cracking was not sufficiently reduced to warrant further work with these materials. Mica was used as a filler in formulations 20-23, and quality of the coating was improved. In flame tests, however, lower char formation and higher flame spread ratings resulted using mica.

Results of these studies indicate that B-1550 resin would be the primary additive of choice for flame spread resistance when used in latex/MS intumescent wood coatings, while FR-300 would be the preferred additive for use in intumescent coatings for steel. Best overall performance, however, was obtained in compositions containing both additives. Formulations 16 and 17, containing 30 parts FR-300 and 30-50 parts B-1550 resin showed excellent flame spread resistance when applied to wood, and afforded a

reasonable degree of insulation protection to steel in 30-minute flame exposure test.

While these systems come close to meeting the intumescent performance objectives of this program, the quality of such coatings needed further improvement. Mud-cracking, the formation of small cracks in the coating surface during drying, was not considered to be a major problem on the wood substrate. Mud-cracking and coating discoloration was, however, observed in varying degree in formulations applied to steel substrates.

Other coalescing aids and plasticizers frequently used to assist in the film forming process during drying of latex coatings were screened as additives for reducing mud-cracking and improving coating quality. Standard formulations, both unmodified and containing FR-300 and/or B-1550 resin, were modified with 5-10 parts of the following plasticizers/coalescing aids: Monoplex DDA, Monoplex DDS (both from Rohm and Haas), Benzoflex 9-88, Benzoflex 50 (both from Velsicol), Texanol (Eastman Chemical), diethylene glycol n-butyl t-butyl ether, diethylene glycol n-butyl ether acetate, and glycol ethers DOWANOL DB and DOWANOL DE (Dow Chemical). While in some cases the use of certain of these plasticizers significantly reduced mud-cracking, this was accompanied by loss of coating adhesion and generation of excessive void space beneath char surfaces during flame exposure.

7. Substrate Treatments

As mentioned above, formulation development led to compositions showing good coating quality and excellent intumescent performance when applied to

wood panels. Certain compositions also exhibited good intumescent performance on steel substrates, but coating quality was considered to be less than desirable. Freshly coated and dried latex/microsphere formulations generally exhibited two undesirable characteristics when applied on steel. The coatings, which normally were cream-colored on wood, took on a yellowish-tan appearance on cleaned steel substrate. The dried coatings on steel exhibited considerable mud-cracking, reflecting a need for better coating film formation by the latex. While use of certain plasticizers and coalescing aids tended to reduce mud-cracking and improve film formation, this was accompanied by poorer coating and char adhesion, and reduced flame insulation characteristics.

The nature of the coating/substrate interface was examined by lifting freshly-dried latex/microsphere coatings from cleaned steel test panels with a spatula. It was found that rusting had occurred beneath the coating surface during the drying process. This was observed with a number of formulations, all containing saran latex. In considering the nature of the saran latex binder used in this work (low pH ~ 2, possibly containing some HCl, and capable of dehydrohalogenation to generate more HCl), this type of flash rusting would not be unexpected when coating steel with saran latex. It is reasonable that this substrate corrosion would lead to reduced coating and char adhesion, and it is quite possible that iron chloride and/or other corrosion products could interfere with latex film formation, with poorer film quality and reduced intumescent performance as a result.

Final studies in the program were thus directed toward eliminating flash rusting by means of (a) use of formulation additives for reduced flash

rusting and (b) wash treatments and use of primers for improved corrosion resistance.

In the additive study, butylene oxide and diethyl tin di-2-ethylhexylmaleate, both of which have been used as HCl scavengers, were added at the 0.5% level to 70/30/30 latex/microsphere/FR-300 formulations using Thickener L, and formulations were applied to cleaned steel panels. Panels were also coated with the base composition above, wherein formulation pH had been raised to 6 (with ammonia), and with a composition raised to pH 8 and modified with 0.3% barium metaborate. This compound has been recommended as an additive for use in reducing flash rusting in aqueous coatings. Observations on coating quality and performance in 15-second flame exposure testing are listed in Table XVI. Neither butylene oxide nor the tin compound improved the coating quality. While raising formulation pH and using sodium metaborate led to some improvement in coating quality, intumescent performance was not improved; time to 1000°F backside temperature was only 4.1 minutes for the metaborate-modified composition when tested in the 30-minute flame exposure test.

Preliminary investigations on substrate pretreatment were carried out by applying several latex/microsphere formulations to steel panels which had received a prior 5 mil (dry) coating of MIL-P-17970C (Navy Formulation 124) paint, a solvent-based halogenated alkyd composition. A very substantial improvement in coating quality was noted in all compositions applied to panels receiving this primer treatment. Yellowing of the coatings was greatly reduced, and mud-cracking did

TABLE XVI

EFFECT OF FORMULATION VARIATIONS ON APPEARANCE AND 15-SECOND
FLAME EXPOSURE TESTING OF SARAN LATEX/SARAN MICROSPHERE
INTUMESCENT COATINGS

Standard Formulation:	Saran Microspheres XD-8217	30 pbw
	Saran Latex SL-143	70 pbw
	FR-300	30 pbw
	"L" Thickener	0.6 pbw

Coatings (8-10 mil dry) applied to cleaned untreated steel panels.

1. 0.5% butylene oxide

No improvement, discoloration, cracks, fair adhesion to panels. High char, small amount of void space beneath char surface.

2. 0.5% dioctyl tin di-2-ethyl hexyl maleate

Similar to above in appearance on panels. panels. Moderate char, large cracks

3. No additive, pH of coating raised from 2 to 6

Slight improvement over 1 and 2 in appearance. Moderate char, large cracks, void space.

4. 0.3% barium metaborate (pH adjusted to 8 from original 2)

Less discoloration, fair adhesion, no cracks in dry coating. High char, large cracks, with void space.

not occur. Three different latex/microsphere compositions were applied
to steel panels with and without Navy 124 pretreatment, and were tested
for 30-minute flame insulation performance. As seen from results in
Table XVII, all compositions performed poorly in the flame testing; the
short time elapsed before failure reflects premature separation of char
from the steel panels, whether precoated or not.

These results supported our speculation concerning coating quality and
flash rusting, since intumescent coatings applied to primed panels showed
good appearance. Failure of primed panels in the flame test occurred
because adhesion of intumescent topcoat to the Navy 124 paint was not
adequate; this is not surprising due to the difference in basic composition
between the solvent-based alkyd precoat and the aqueous latex topcoat.
This problem might be solved by a different alkyd primer, formulated
for adhesion by the aqueous top coat.

In concluding the laboratory development work on the project, panel pre-
treatment studies were continued with efforts to find surface treatments
for optimum coating appearance and intumescent behavior. Steel panels
pretreated with a variety of inorganic wash treatments and organic primers
were topcoated with latex/microsphere intumescent coating. Char forming
characteristics of coated panels were observed by 15-second flame exposure,
while insulation characteristics were measured by the 30-minute flame
impingement test. The 70/30/30 latex/microsphere/FR-300 composition using
Thickener L was used as the intumescent topcoat. Pretreated panels were
coated with 36 mils of wet formulation, and air dried to give the final

TABLE XVII

THERMAL INSULATION PERFORMANCE OF LATEX/MICROSPHERE COATINGS USING STEEL PANELS PRECOATED WITH NAVY 124 PAINT

Panel Treatment: 5 mils (dry) MIL-P-17970C, air dried, followed by 36 mils (wet) latex/microsphere coating, air dried.

Panel	Precoated With Navy 124	Latex/MS* Coating Formulation	Steel Panel Test, Time To 1000°F
1	Yes	None	1.8
2	No	70/30 Latex/MS	2.5
3	Yes	70/30 Latex/MS	3.0
4	No	70/30 Latex/MS + 30 pts FR-300	2.3
5	Yes	70/30 Latex/MS + 30 pts FR-300	1.8
6	No	70/30 Latex/MS + 30 pts FR-300 + 30 pts B-1550	3.3
7	Yes	70/30 Latex/MS + 30 pts FR-300 + 30 pts B-1550	2.6

*Formulations contained ∿ 0.5% Thickener L

topcoat thicknesses of 8-10 mils. Types of steel panel pretreatment and results from flame exposure testing are listed in Table XVIII.

On the basis of 30-minute flame impingement testing, best performance was shown by coated panels receiving Bonderite 37 (zinc phosphate) pretreatment. Using time/temperature profiles as a guide, order of performance based on substrate pretreatment is as follows: Bonderite 37 > MIL-I-3420A > Untreated Steel > Metabond > HA-8 > Bonderite 1000 > Sandblasted Steel. For all remaining panels tested, time elapsed to reach a backside temperature of 1000°F was four minutes or less. It is interesting to note that except for the Bonderite 1000-treated panel, chars did not separate from the panels listed above during testing. Of further interest is the fact that except for the panel primed with HA-8 acrylic latex, all panels listed above were pretreated with inorganic washes rather than with organic-based primer systems.

All panels not listed in the paragraph above were treated with polymeric organic primer systems. In most cases separation of char from these panels occurred during the 30-minute flame test, with poor intumescent coating performance as a result. Use of organic primers, however, generally resulted in improved coating appearance, with less yellowing of the coatings and less mud-cracking of the coatings during the drying process.

When intumescent coatings were applied to aluminum or galvanized substrates, adhesion ranged from poor to good, but char formation was low and was accompanied by severe char cracking, leaving a considerable portion of the substrate surface exposed.

TABLE XVIII -- Part 1. SUBSTRATE PRETREATMENT AND EFFECTS ON PERFORMANCE OF SARAN LATEX/
MICROSPHERE INTUMESCENT COATINGS

Coating Formulation (Dry Basis):
Saran Microspheres XD-8217	30 pbw
Saran Latex SL-143	70 pbw
FR-300 (Decabromodiphenyl Oxide)	30 pbw
Thickener "L"	0.6 pbw

Panel Number	Surface Treatment	Coating Quality and 15-Second Flame Test Observations	30-Minute Flame Insulation Test Time (Min) to Reach			Char Failure
			1000°F	1050°F	1100°F	
1	None	Cracks in coating after drying. Fair adhesion. After flame exposure, high char with voids under surface, but more dense than when using plasticized formulations.	3.9	24	>30	No separation
2	Bonderite 37 (Zinc Phosphate)	Similar to No. 1	>30	>30		No separation
3	Bonderite 1000 (Iron Phosphate)	Similar to No. 1	5	8.5	9.0	8.3 Minutes
4	Metalloid	Similar to No. 1	2.9	8.0	27	No separation
5	Galvanized Steel	Good coating appearance, no cracking, fair adhesion. Low char, large cracks upon flame exposure.	1.2	1.3	<2	No separation
6	Sandblasted Steel	Similar to No. 1	2.3	3.1	9	No separation
7	MIL-I-3420A	Similar to No. 1	4.5	30	>30	No separation
8	Navy 124	Good coating appearance, no cracking, poor adhesion to basecoat. Low char with large cracks upon flame exposure.	1.2	1.3	<2	0.5

TABLE VIII -- Part 2.   SUBSTRATE PRETREATMENT AND EFFECTS ON PERFORMANCE OF SARAN LATEX/
MICROSPHERE INTUMESCENT COATINGS

Coating Formulation (Dry Basis):   Saran Microspheres XD-8217   30 pbw
                                    Saran Latex SL-143   70 pbw
                                    FR-300 (Decabromodiphenyl Oxide) 30 pbw
                                    Thickener "L"   0.6 pbw

Panel Number	Surface Treatment	Coating Quality and 15-Second Flame Test Observations	30-Minute Flame Insulation Test Time (Min) to Reach			Char Failure
			1000°F	1050°F	1100°F	
9	Navy 84, 2 mils (TT P645)	Good appearance, adhesion, no cracks Low char, large cracks upon flame exposure	1.4	1.6	<2	1.0
10	Mil P152338 Wash, 2 mils	Similar to No. 9	1.4	1.5	<2	1.1
11	Mil P-24441 Primer, 3 mils	Similar to No. 9	1.6	1.7	<2	<1
12	XD-8609.01 Vinylidene/Buta-diene Latex, 6 mils	Fair adhesion, but cracks in dry coating. Low char, large cracks from flame exposure.	1.7	1.8	<2	1.3
13	2:1 D.E.R. 331/ D.E.H. 14 Epoxy Resin, 5 mils	Good adhesion, cracks in dry coating. Low char, large cracks from flame test	2.1	2.3	4	No separation
14	DL-615 S/B Latex, 5 mils	Good appearance, no cracks, fair adhesion Low char, large cracks from flame test	1.9	3.1	3.5	1.5
15	DL-283 S/B Latex 6 mils Dry	Similar to No. 12	2.7	2.9	3.5	2.8

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TABLE XVIII -- Part 3. SUBSTRATE PRETREATMENT AND EFFECTS ON PERFORMANCE OF SARAN LATEX/
MICROSPHERE INTUMESCENT COATINGS

Coating Formulation (Dry Basis):

Saran Microspheres XD-8217	30 pbw
Saran Latex SL-143	70 pbw
FR-300 (Decabromodiphenyl Oxide)	30 pbw
Thickener "L"	0.6 pbw

Panel Number	Surface Treatment	Coating Quality and 15-Second Flame Test Observations	30-Minute Flame Insulation Test Time (Min) to Reach 1000°F	1050°F	1100°F	Char Failure
16	HA-8 Acrylic Latex (Rohm & Haas), 6 mils	Fair Adhesion, severe cracking of dry coating. Low char, large cracks from flame test.	2.9	9.0	20	No separation
17	Aluminum Panel (2024), no surface treatment.	Good appearance, no cracks, but very poor adhesion. Low char, large cracks in flame test.	--------Not Tested--------			--------
18	Aluminum Panel, Alodine treatment	Good appearance, good adhesion, no cracking. Low char, large cracks in flame test.	--------Not Tested--------			--------

Results from these studies indicated that organic primers may be of use
in improving quality and appearance of saran latex/MS coatings applied
to steel substrates, but their use results in loss of intumescent performance
properties. The inorganic wash pretreatments (e.g., Bonderite) for panels
resulted in improved intumescent performance over untreated panels. It
should be pointed out, however, that flash-rusting was still observed
beneath coating surfaces and mud-cracking occurred as the coatings dried on
these panels. It would appear that such treatments upgrade coating
adhesion sufficiently to improve flame insulation performance, but further
work with either primer systems or formulation modifiers for improved
coating quality and appearance would be recommended prior to commercial
use of latex/microsphere coatings for fire protection of steel. For
maximum thermal insulation characteristics, Bonderite 37 (zinc phosphate)
appears to be the best metal pretreatment for use with microsphere-based
intumescent coatings.

When applied to zinc phosphatized steel, the SL-143/MS/FR-300 coating
meets with the primary performance requirement of the present study
in maintaining panel backside temperature below 1000°F for 30 minutes
during flame exposure. Time/temperature profiles of the latex/micro-
sphere formulation on treated and untreated steel are compared with
epoxy resin-based intumescent paint (MIL-C-46081) in Figure 15. The
epoxy system performs well within the 1000°F/30-minute test limits,
and provides a somewhat greater degree of insulation (about 100°F lower
backside temperature over the test period) than the microsphere system.
In comparing the relative merits of either system, however, consideration

FIGURE 15

INTUMESCENT COATINGS - 30 MINUTE FLAME EXPOSURE
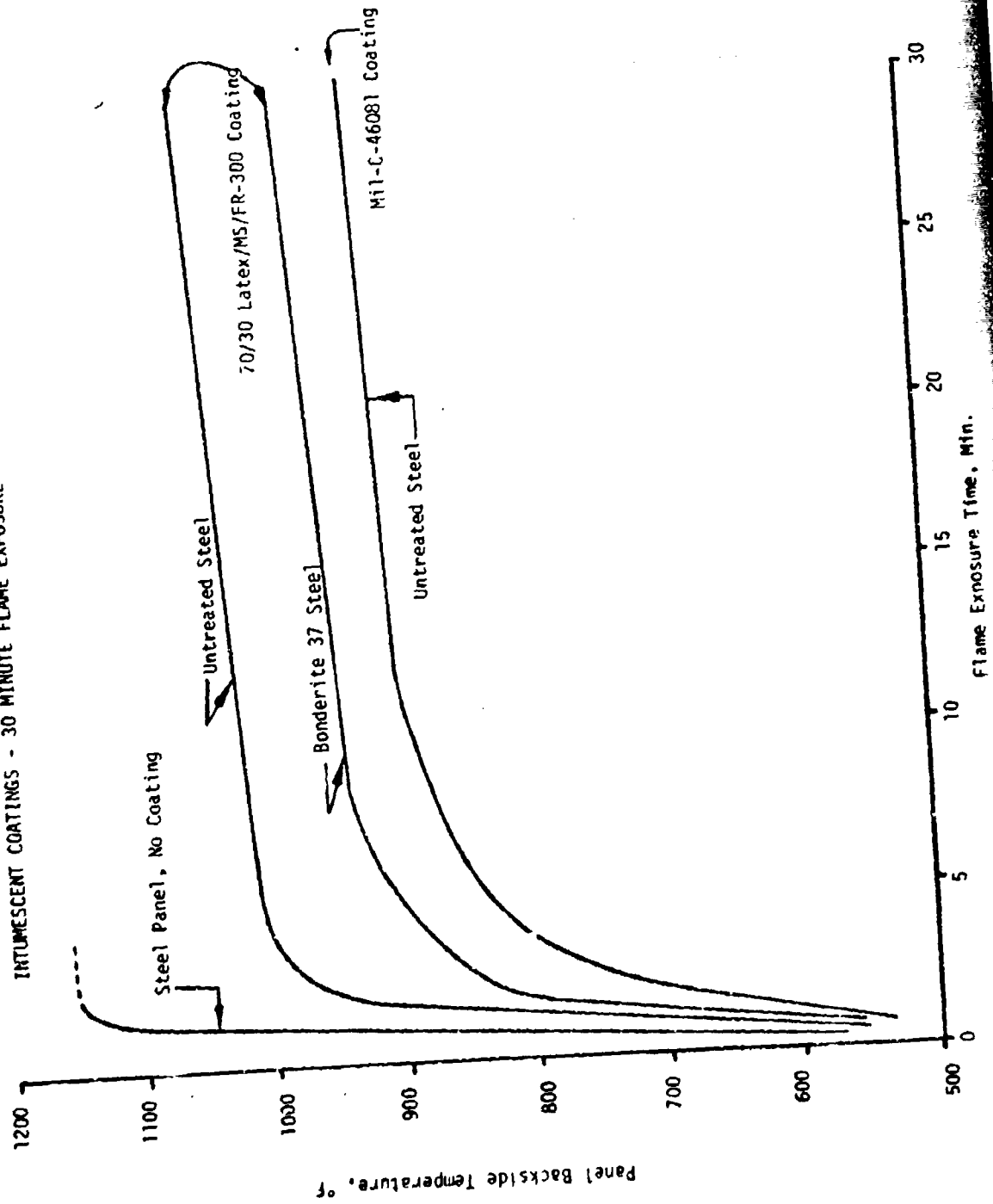
should be given to environmental and handling aspects in using a
two-component, solvent-based paint versus the single component, water-
based coating of the present work.

VI. Conclusions and Recommendations

These studies have established the feasibility of using saran microspheres in water-based intumescent coatings for fire protection, thus meeting the program goal. Early in the program, it was concluded that while microspheres serve as an essential formulation component for intumescence, variations in type of binder and use of flame retardant additives appear to have equal if not greater impact on overall flame retardant properties than variations in microsphere polymer composition.

Advanced formulation studies carried out using a commercial grade microsphere product in combination with a saran-type latex and certain halogenated flame retardant formulation modifiers led to the development of aqueous coatings having excellent intumescent performance and good coating quality when applied to wood substrates. When applied to steel panels receiving a zinc phosphate pre-treatment, coating compositions based on saran microspheres, saran latex, and decabromodiphenyl oxide provide sufficient intumescence and flame insulation to maintain steel panel backside temperatures below 1,000°F over a 30 minute flame exposure period, thus meeting the primary performance objective of the program. On the basis of this test, intumescent/insulation performance of this water-based composition is considered to be comparable with that observed during testing of a solvent-based MIL-C-46081 paint.

Coating quality, adhesion, and appearance of latex/microsphere compositions do not compare favorably with that of MIL-C-46081 type paint when applied to steel substrates, however, and further development work would be recommended. Optimum coating quality, appearance, and intumescent performance in compositions of the present work, when applied to steel, would require studies to identify a primer system which would protect the substrate from flash-rusting due to low binder pH, while maintaining good adhesion to the intumescent topcoat. Latex/microsphere compositions developed in this program are considered to be ready for such further development by a knowledgeable paint formulator/supplier.

VII. Appendix

APPENDIX VIIA.   Experimental Procedures

1. Microsphere Polymerization Techniques

Laboratory procedures used in microsphere preparation by limited
coalescence polymerization techniques were adapted from those described
in patent literature[3]. A sample procedure and typical recipe are
described below.

All polymerizations were carried out in citrate bottles. Agitation was
provided by tumbling the bottles at 22 rpm in a thermostated bath. The
water phase polymerization component was made up by adding to 100 parts
of deionized water (1) 15 parts of a 30 percent by weight colloidal
silica dispersion, (2) 2.5 parts of a copolymer prepared from diethanol-
amine and adipic acid in equimolar proportions to give a product
viscosity of 5 cps at 25°C, (3) one part of a solution containing 2.5
percent potassium dichromate, and (4) enough hydrochloric acid to
adjust the mixture to a pH of 4. The oil phase mixture contained 70
parts of vinylidene chloride, 30 parts acrylonitrile, and 1 part of
divinylbenzene catalyzed with one-half to one percent of 2,2-azobisiso-
butyronitrile. To this monomer mixture was added 12 parts of isobutane.
Sixty-five parts of the oil phase were added to the water phase and
subjected to extremely high agitation by a blade rotating at a speed of
about 10,000 rpm. This mixture was then placed in the polymerization
vessel and sealed. The reaction mixture was maintained at a temperature
of about 50°C for a period of 24 hours.

Some changes in the water phase of the above example were necessary for successful polymerization of certain monomer combinations. Addition of sodium chloride, use of a "co-suspending" agent and variations in the level of colloidal silica and of the copolymer of diethanolamine and adipic acid were typical water phase alterations.

2. Coating Formulation Techniques

For typical formulations, latex was weighed into a container and wet cake microspheres were then added, using an air stirrer for agitation. This was then followed by addition of mineral fillers or salts, when used. Use of such materials required stabilization of the latex with a surfactant (e.g., DOWFAX 2A0 at 2-4 parts) to insure complete dispersion. When using organic flame retardant additives (e.g. FR 300, B-1550 resin), it was found necessary to add these components to the latex prior to adding the microspheres. When used, coalescing aids, surfactants, and plasticizers were also added to the latex prior to adding microspheres. In the final compounding step, thickeners were added to the formulations for proper coating rheology.

3. Preparation of Test Panels

A major part of testing was carried out with coatings applied to either clean untreated or Bonderite 37 (zinc phosphate) treated 24 gauge 4" x 12" steel panels. The panels were kept in vendor's protective wrapping until used, and were handled in a manner to avoid fingerprints and other surface contamination. In most of the work, intumescent

coatings were applied with a 36 mil draw bar, 3" in width. These 36-mil wet coatings were then dried at room temperature for 4-5 days. Panels having a dry coating thickness of 8-10 mils were taken for further testing. For flame insulation testing, coatings were applied to panels to which a type K thermocouple had been spot-welded in the center of the back (uncoated) side.

When primers were applied as a basecoat, the dry coatings ranged from 3 to 6 mils in thickness, depending on the primer. These were also air-dried for 4-5 days before subsequent application of the intumescent coating.

Intumescent coatings were also applied to 1/4" x 4" x 24" marine plywood panels. Normally, the coatings were applied with the 3" wide 36-mil draw bar, giving a dry coating of 8-10 mils in thickness after air-drying for 4-5 days.

4. Flame Testing Procedures

A two-foot tunnel flame spread test (ASTM-E84) was used to measure intumescent performance of coatings applied to plywood test panels. A test panel is placed coated side down in a two-foot test chamber, wherein the panel is inclined at a 28° angle from horizontal. An asbestos and steel backing plate is placed over the back side of the panel, and the coated side of the panel is then exposed to flame at its lower end. The flame source is a gas-fired Fisher burner equipped with a pressure regulator. The burner is positioned with

its top 1 3/8" below the panel, at a point 2 3/4" away from the end of the panel. The flame spread is a measure of the extent of travel of a flame front across the surface of the inclined sample. The position of the flame front from the lower end of the panel is recorded (in inches) every 15 seconds after initial flame exposure for a four-minute period. After an additional one-minute burning period, the flame is turned off, and after-burning characteristics are noted. The rating obtained by this test is determined by maximum travel of the flame up the panel, and is based on testing of two standard reference materials which have been assigned arbitrary flame spread ratings. Flame spread rating is expressed as a percentage of the difference between these two materials. Increasing resistance to flame spread (and hence, improved flame retardant behavior) is characterized by lower flame spread ratings; a flame spread rating of zero is arbitrarily assigned to materials which do not burn in the presence of flame.

Two types of flame testing were used in work with coated steel panels. A 15-second flame exposure test was used for screening purposes, and a 30-minute flame impingement test was employed for a measurement of flame insulation protection of steel panels. These procedures are reviewed in detail in Section IV.

APPENDIX VIIB. Microsphere Polymerization Studies: Composition Versus
Foaming Properties

1. Vinylidene Chloride/Acrylonitrile Compositions

Figure 4 from the previous section, appendix Figures VIIB-1 and 2, and
appendix Table VIIB-I illustrate the effects of composition on foaming
properties of vinylidene chloride/acrylonitrile-based microspheres.
Foam collapse temperature (Figure 4) first increases and then levels
off with increasing acrylonitrile concentration. Taking into account
effects due to blowing agent, foaming temperature (Table VIIB-I) also
increases with increasing acrylonitrile concentration, until a
relatively constant value is achieved.

No effect on foam collapse temperature due to variation and type of
blowing agent was observed. Some effects due to divinylbenzene (DVB)
have been noted and are discussed below.

Figures VIIB-1 and 2 demonstrate the effect of temperature and composition
on foamed density. For the several different compositions shown in
Figure VIIB-1, foamed density first decreases to a minimum (maximum foam
volume) and then increases with rising temperature. Compositional
influences are apparent as a shift in the optimum foamed density occurs
(minimum in the foamed density versus temperature) with changes in
VCN concentration.

FIGURE VIIB-1

Foamed Density as a Function of Foaming
Temperature for Vinylidene Chloride/Acrylonitrile Microspheres

FIGURE VIIB-2

Effect of Divinylbenzene on the Foamed
Density of Vinylidene Chloride/Acrylonitrile Microspheres

155°C Foamed Density vs DVB
concentration for compositions
having a 43/57 vinylidene
chloride/acrylonitrile monomer
ratio
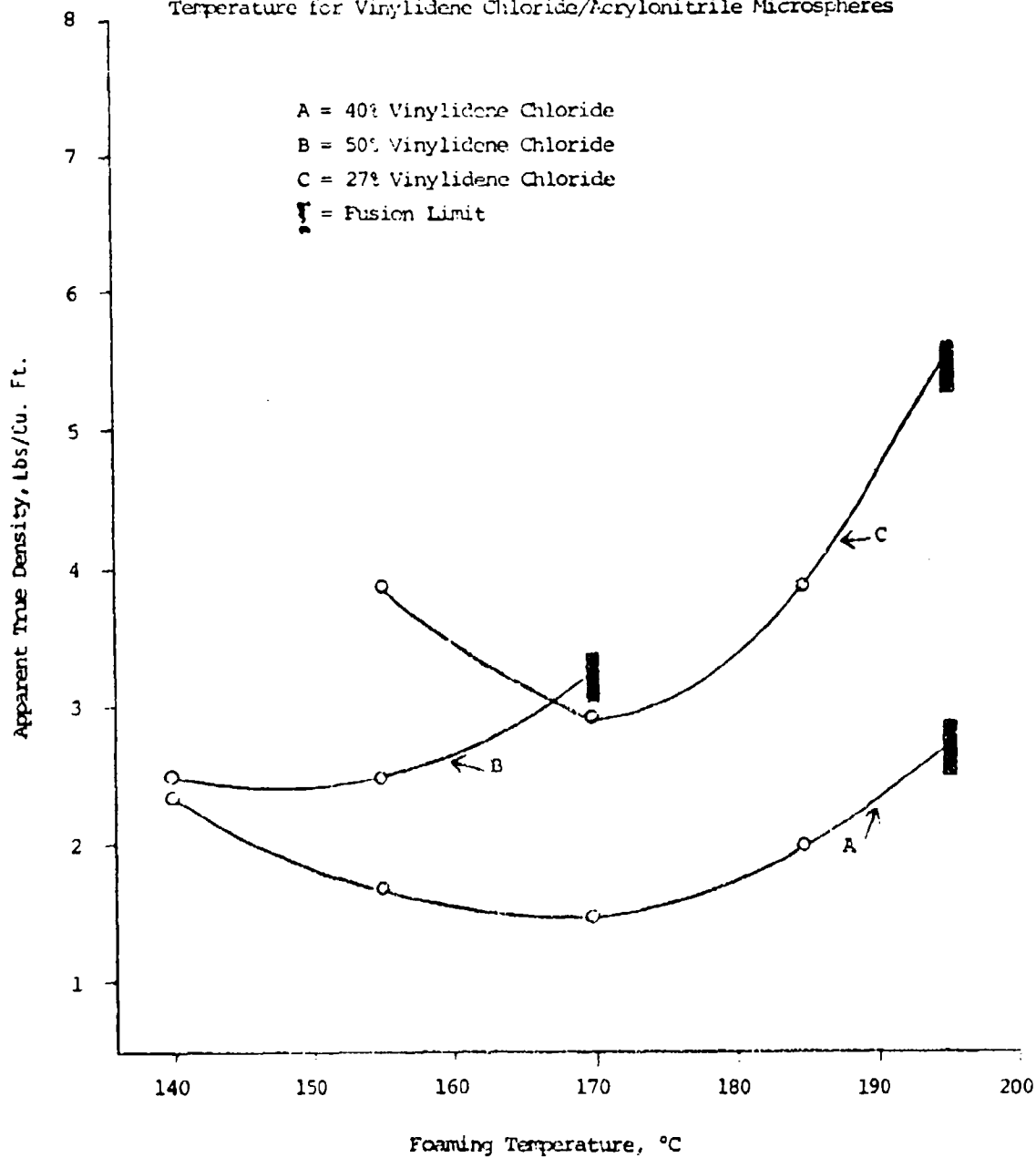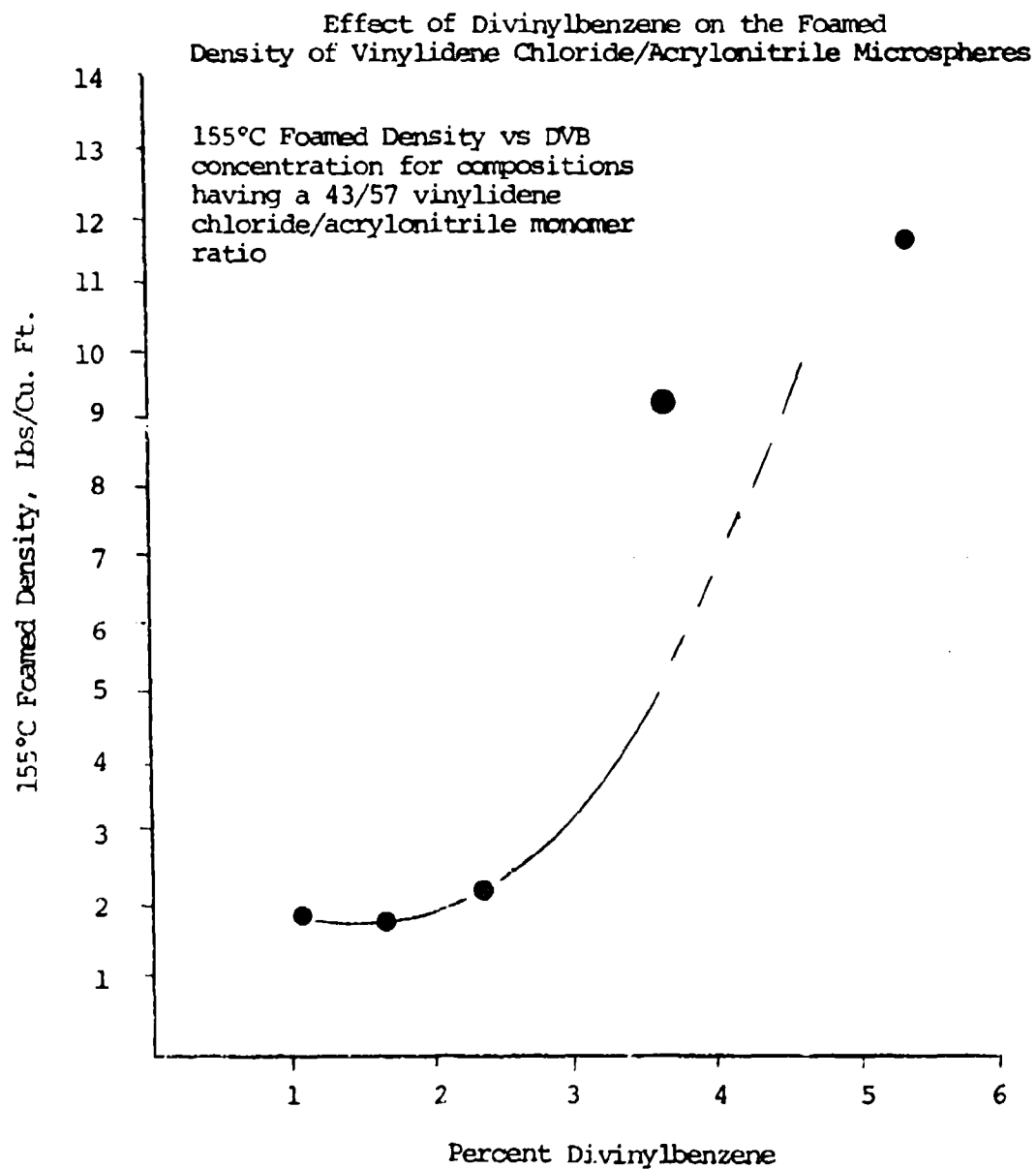
TABLE VIIB-I

Effect of Monomer Ratio and Blowing Agent
On Foaming Behavior

Vinylidene Chloride/ Acrylonitrile Ratio	Blowing Agent	Foaming Temperature	Foam Collapse Temperature
74.5/25.5	Isobutane	83.3°C	133°C
	Neopentane	92	136
	2, 3 dimethylbutane	102-107	144
	Freon 114	93-103	140
64/36	Isobutane	95	152
	Neopentane	100	165
53/47	Neopentane	100	175
43/57	Neopentane	110	190
32/68	Neopentane	119	(?)
29/71	Neopentane	113	193

The response of foamed density to DVB concentration is shown in
Figure VIIB-2. Note the increase in foamed density with increasing
DVB. This effect is not unexpected because of the well-known effects
of cross-linkers in other foam systems[4]. Based on observations of
foamed polystyrene[4], foamed density would be expected to decrease to
an optimum and then increased with increasing DVB. Failure to observe
this phenomenon is probably due to the limited data obtained.

2. Monomer Systems with Styrene

The compositions based on styrene and acrylonitrile do not have much
variability in foaming or foam collapse temperature. Figure VIIB-3
shows the relationship between foam collapse temperature and acrylonitrile
content for styrene/acrylonitrile compositions. Because the maximum
collapse temperature appeared to be so low (155°C) and compositional
effects are relatively small, a thorough study of the systems was not
attempted.

3. Other Monomer Systems

Other monomers listed in Table III (from the previous section) were
selected for screening as possible components of a microsphere with
improved high temperature foaming properties. Various combinations
of these monomers, selected for high temperature properties, were
polymerized. Table VIIB-II lists better compositions and foam collapse
temperatures for the systems which successfully polymerized. Of these,

FIGURE VIIB-3

Collapse Temperature in Styrene/
Acrylonitrile Microsphere Compositions
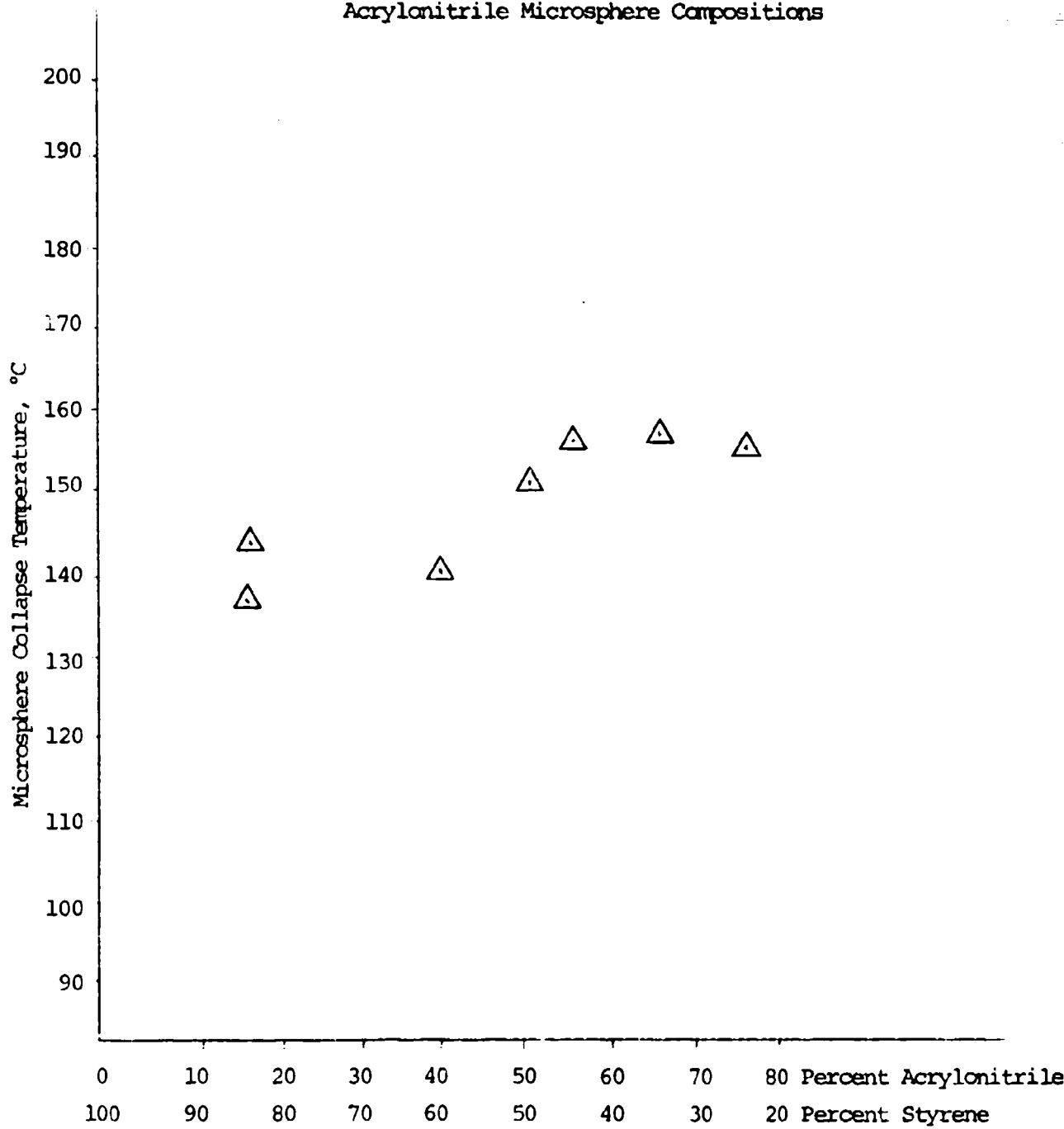
TABLE VIIB-II

Microspheres Prepared From Miscellaneous Monomers

Monomers Used: Acrylonitrile (VCN), Methacrylonitrile (MAN),
Styrene (STY), Methyl Methacrylate (MMA),
t-Butyl Styrene (TBS), N-vinyl-2-pyrrolidone (NVP),
and t-Butyl Acrylamide (TBAM).

Monomers	Composition	Conversion	°C Foam Collapse
STY/MMA	20/80	Yes	140-150
STY/VCN	40/60	Yes	145-150
STY/VCN/MAN	35/55/10	Yes	155-157
VCN/TBAM/MAN	70/20/10	Yes	178-182
VCN/TBAM/VDC	70/20/10	Yes	170-185
TBS/VCN	—	Poor	--
TBS/VCN/MAN	—	Poor	--
NVP/STY	--	Poor	--
NVP/VCN	--	Poor	--

none yielded properties better than the vinylidene chloride/acrylonitrile systems, although compositions based on t-butyl acrylamide appeared promising. Unfortunately, the limited solubility of solid t-butyl acrylamide in other monomers restricted its maximum concentration to 20%.

Co-suspending agents were investigated as a means to improve microsphere suspension stability. Suspension failures resulted when polyvinyl alcohol or the dihexyl ester of sodium sulfosuccinic acid were added after homogenization. Successful polymerization resulted when METHOCEL or colloidal alumina were added. All properties, including particle size and shape and foaming characteristics, appeared normal for microspheres polymerized using colloidal alumina. Microspheres made with METHOCEL, however, were abnormally small and could not be foamed. The smaller relative size of the METHOCEL stabilized particles is undoubtedly due to the ability of this material to prevent recoalescence (as in suspension polymerization). No explanation has been found for the inability to foam these microspheres.

APPENDIX VIIC. Morphology and Thickener/Plasticizer Study - Intumescent
Coatings with Saran Microspheres

A method for microscope study of coating cross section was developed
using a formulation prepared as follows:

	Wet Weight	Dry Weight
DL 233 (Dow Styrene/Butadiene Latex)	120	60
XD-8217 (Saran Microspheres)	48	30
Celite 281	-	10
Alcogum 5950 Thickener	10	0.5
Igepal CO 630 Wetting Agent	2	0.5
	180	110.0

(Total Solids - 61.7%)

Small amounts of dyes wet out with Igepal CO 603 and dispersed in water
were added to the formulation. Dyes used were:

Ciba-Geigy Irgacet Red 3G1

"   "   "   Yellow 2G1

"   "   "   Brill Blue 2G1

Drawdowns (10 mils wet) were made on a coated fiber board and expanded
wet by heating for 10 minutes in an oven at 275°F. Other drawdowns
were prepared and allowed to air dry. Pieces of coating were cut by
razor blade, lifted from the surface of the fiber board, and mounted
edgewise on a microscope slide. Coating thickness was then studied

in a Leitz microscope using incident light. Dyes helped to distinguish the microspheres from latex. Yellow and blue were somewhat better than red for contrast.

After cutting a coating piece from the surface, the best edge for observation was obtained by snapping rather than cutting. A sharper surface was obtained by freezing the piece before breaking or snapping.

Expansion Characteristics of Coating

A saran microsphere/saran latex coating formulation was prepared as follows:

	Content (Solids)	
SL 143	70%	Diluted to 45% and thickened with Alcogum 5950
XD-8217	30%	

Yellow dye as needed

Drawdowns (30 mils wet) were made on a Teflon plate and a coated fiber board and allowed to air dry. The coating was removed from the Teflon plate prior to heat foaming in order to allow free expansion of micro-spheres in all directions through the sample. Coatings were allowed to stay in place on the fiber board substrate. Heat foaming of coated board would allow expansion in coating thickness (Z-direction expansion), but expansion in area (X and Y direction) would be restricted.

The fiber board was cut in several pieces and the coating expanded at 275°F for 2, 4, 6, 8, 10 and 12 minute periods. Maximum expansion at 4 to 10 minutes was from 23 to 40 mils or about 2x. Microsphere distribution by microscope examination showed uniformity through the cross section.

The dried film which had been lifted from the Teflon plate was broken in small pieces about 2" x 2" and expanded in an oven at 1, 1 1/2, 2 and 3 minutes. Area increase was 5x at 2 minutes and thickness increased 2.6x or a volume increase of 12.9x.

Microspheres in the expanded free film were spherical by examination of the cross sectional area. In the fixed coating, microspheres were elongated with the Z direction. Since the film was adhered to the substrate, much less expansion in the X and Y direction occurred due to restricted ability of the film to expand area-wise.

Expansion With Other Thickeners

Thickener L (G.A.F.) and Elvanol 5105 (polyvinyl alcohol, du Pont) are often used with saran latex. These materials were tested in comparison with Alcogum 5950 to determine effect of thickener type on efficiency of microsphere expansion under controlled foaming conditions. Three formulations were prepared as described below:

	% Solids	Dry %	Wet Wt. (g.)
SL 143	58	70	241.4
XD-8217	62	30	96.8
Yellow dye as needed			(338.2)

1. Elvanol 51-05 (148 cps) added 14 g., 5% solids
2. Thickener L (280 cps) added 3.5 g., 15% solids
3. Thickener L (8000 cps) added 8.5 g., 15% solids

Thirty mil wet 6" x 12" drawdowns were made on coated fiber board using the above saran latex formulations for comparison with the previous Alcogum-thickened formulation. Boards were cut in pieces and expanded at 275°F as described previously.

EFFECT OF THICKENER ON FOAMING CHARACTERISTICS

	Alcogum	Thickener L 3.5 g.	Thickener L 8.5 g.	Elvanol 51-05
Coat weight, wet, g/72 in^2	2.8	30.2	34.9	30.2
Coat weight, dry	12.6	17.8	20.6	17.8
Coat weight, dry, g/in^2	0.175	0.247	0.286	0.247

Dry Coating Thickness - mils

	Alcogum	Thickener L 3.5 g.	Thickener L 8.5 g.	Elvanol 51-05
Unexpanded	20	19	23	22
Expanded - 1 Minute	27	64	50	50
2	33	65	55	58
3	37	63	60	60
4	35	62	60	57
6	34	65	51	55
8	37	67	75	62
10	39	62	62	60
12	38	58	63	58
Maximum expansion - mils	19	58	52	40
mils/gm/sq. in.	108.6	234.8	181.8	161.9

These coatings were examined by microscopy as previously described.

Results:

Alcogum Thickener   - Unexpanded: good MS distribution, some voids, air pockets.

                          - Expanded: microspheres and voids elongated in Z direction.

Thickener L (280 cps) - Unexpanded: good MS distribution, many voids.

                          - Expanded: MS and voids elongated in Z direction.

         (8000 cps) - Unexpanded: good distribution, few voids.

                          -- Expanded: MS and voids elongated.

Elvanol 50-05   - Unexpanded: good distribution, few voids.

                          - Expanded: MS and voids elongated.

Plasticizer Addition to Coating

Igepal CO 630 has been reported to act as a plasticizer on saran latex. This additive was investigated to determine if more foaming volume can be obtained through use of latex plasticizers to lower the binder resistance to microsphere expansion. The following formulations were prepared:

Formulation Number		Solids %	Weight Grams	Dry Solids Weight
1	SL 143	58	120.7	7.0
	XD-8217	62	48.4	3.0
	Thickener L	15	6.0	0.9
	Dye	10	10.0	1.0
		55.05	185.1	101.0
2	No. 1 + Igepal CO 630	25	12.0	3.0
		53.22	197.1	104.9
3	SL 143	58	120.7	7.0
	XD-8217	62	48.4	3.0
	Alcogum 5950	5	10.0	0.5
	Dye	10	10.0	1.0
		53.68	189.1	101.5
4	No. 3 + Igepal CO 630	25	12.0	3.0
		51.96	201.1	104.5

Drawdowns were made as described earlier and coatings were expanded in a similar manner. Results of foaming efficiency studies are given below:

EFFECT OF PLASTICIZER ON FOAMING CHARACTERISTICS

Formulations

	Thickener L	Thickener L + CO 630	Alcogum 5950	Alcogum + CO 630
Wet Weight, g.	34.0	22.0	30.5	26.7
Dry Weight, g.	18.7	11.7	16.4	13.9
Coat Weight, g./in^2	0.26	0.16	0.23	0.19
Maximum Expansion, mils	75.0	58.0	65.0	53.0
mils/g./sq. in.	288	362	283	279

Microscope examination of these coatings showed that the formulation containing Igepal CO 630 had a substantial amount of air trapped in the coating. This could be expected to cause spots or faults in the expanded coating, since these voids are not sealed during the expansion process.

Conclusions

1. Microspheres were well dispersed throughout the coating thickness. No problems with nonuniformity of MS distribution were seen.

2. With 30% microspheres in the coating, free expansion of saran latex-based films will give a volume expansion of about 12-13 times. When kept oriented in Z direction expansion (i.e., when foamed while adhered to a substrate), volume increase is at best 3 to 3.5 times.

3. Expansion in the Z direction orients the microsphere walls and voids in the expansion direction. They are no longer spherical.

4. Voids caused by air bubbles, diffusion of isobutane or trapped water will cause a fault or weak spot in the coating, hence formulations should be degassed prior to application.

5. Thickener L and Elvanol appear to allow better expansion than Alcogum.

6. Igepal CO 630 appears to plasticize formulations containing Thickener L , but not Alcogum-containing formulations. Microsphere foaming efficiency is improved with addition of the plasticizer to Thickener L .

7. Effects of thickeners and plasticizers on foam-generating efficiency of microsphere/latex formulations were measured only under controlled 275°F conditions. Flame test conditions are necessary letermine utility of these additives for improving intumescent coating performance.

APPENDIX VIID. References

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3. D. S. Morehouse, U.S. Patent 3,615,972.

4. L. C. Rubens, J. Cellular Plastics 1, pp. 3-12, (1965).